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SLURRY FUEL PERFORMANCE STUDIES

SUMMARY TECHNICAL REPORT

Technical Report AFAPL-TR-66-73

Robert L. Durfee
Atlantic Research Corporation

June, 1966

Air Force Aero Propulsion Laboratories
Research and Technology Division
Air Force Systems Command
Wright-Patterson Air Force Base, Ohio

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FOREWORD

This report was prepared by Atlantic Research Corporation, Alexandria, Virginia, under Air Force Contract AF 33(657)-14336. The contract was initiated under Project No. 3048, "Aviation Fuels", Task No. 304802, "Unconventional Fuels". The work was administered under the direction of the AF Aero Propulsion Laboratory, Research and Technology Division, Wright-Patterson Air Force Base, Ohio. Mr. A. E. Zengel was the Project Engineer.

The report covers the work performed in Phase I of the subject contract, between February, 1965 and February, 1966. Dr. Robert L. Durfee was responsible for the administrative and technical aspects of the program. Mr. William H. Sargent also contributed to the program. Over-all responsibility for the management of the program was charged to Dr. Jack M. Spurlock, Chief of the Engineering Research Group, and Dr. Michael Markels, Jr., Director of the Advanced Technology Department. The number applied to this report is AFAPL-TR-66-73.

This report was submitted by the author June, 1966.

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ABSTRACT

This program was concerned with the development, characterization, and combustion testing of advanced boron slurry fuels for use in low-altitude ramjet-powered missiles. Three types of boron were used: commercial grade; submicron; and ultra-fine, high purity boron. Through extensive ball-milling of the submicron and ultra-fine powders, slurries could be formulated (in ungelled JP-4 carrier) which were competitive with standard commercial-grade formulations in volumetric heat release, rheology, and stability. Other formulation work resulted in the optimization of a 1965 "workhorse" formulation (basic formulation of 73 per cent ball-milled boron in gelled JP-4) and a slurry of washed boron in isopropanol which can be loaded to a maximum solids content of about 80 per cent.

The most critical trade-off among slurry properties is between storage stability and rheology (yield stress and viscosity) at low temperatures. Based on work at the University of Dayton Research Institute, the apparent viscosities of "standard", shelf-stable slurries of 73 per cent boron in JP-4 and 75 per cent boron in isopropanol at 100 sec^{-1} shear rate and -65°F are about 5,000 poise and 4,000 poise, respectively. Reduction of these values appears to be one of the most immediate problems in future boron slurry development.

A particle (agglomerate) size distribution of one to 50 microns was found in slurries containing ball-milled commercial boron. Atomization in the particle mill resulted in mostly particles between 25 and 100 microns in diameter; and atomization in a dual-fluid injector designed for use with the micro-ramjet produced particles mostly between 10 and 50 microns in diameter.

Combustion tests were performed in an ambient-pressure combustor and a 3.5-inch micro-ramjet engine equipped with a particle mill or with a dual-fluid injector. The results of the particle-mill tests established a base-line for comparison of micro-ramjet combustion data with data from

the Marquardt test engine. Trends observed in combustion performance as a function of slurry properties included enhancement of performance corresponding to: a more volatile carrier; smaller particle sizes resulting from atomization; and (possibly) decontamination of the surface. With the dual-fluid injector the slurry containing 70 per cent ultra-fine, high-purity boron performed best by far, indicating a strong enhancement due to the small particle size when the slurry is well atomized.

Very little combustion data were obtained with slurries containing 80 per cent solids, because of dilation of these slurries in the feed system. The two most promising formulations at present are 73 per cent ball-milled boron in gelled JP-4, and 75 per cent ball-milled boron in isopropanol. These two slurries performed similarly in the particle-mill-equipped micro-ramjet engine.

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1.0 INTRODUCTION

1.1 GENERAL BACKGROUND

The complex technology associated with the development and use of boron slurry fuels for low-altitude, ramjet-powered missiles has been a subject of widespread interest for about ten years. Prior to 1964, the primary goals of the research programs concerned with development of boron-containing slurries were to obtain maximum solids loadings at minimum apparent viscosity. This effort[1] has resulted in a number of promising slurry formulations, in the range of 73 to 80 per cent solids (commercial-grade boron), which exhibit desirable rheological properties at room temperature, adequate storage stability properties, and reasonable combustion performance.

Since 1964, the optimization of promising formulations, in terms of stability, rheology, and other properties, has been emphasized.[2] In addition, possible methods of enhancing combustion of the slurries have been investigated.[2] Efforts have been made to understand the various interactions which occur between slurry components, and how these interactions affect slurry properties. This knowledge has aided the optimization of formulation variables in order to obtain desirable properties.

1.2 PROMISING BORON SLURRY FORMULATIONS

Two general types of boron slurries are available: systems in which a gel structure is used to support the solid particles; and "solvated" systems in which the solid particles are held in suspension by relatively strong interactions between the solids and the carrier (no gellant is required). For the gelled systems, which include all the types which consist of a hydrocarbon carrier containing ball-milled commercial grade boron, gelled JP-4 appears to be one of the most promising carriers. Stable slurries exhibiting practicable viscosities (less than 200 poise at 100 sec^{-1} shear rate) at ambient temperature are available over the range of solids loading from 70 per cent to 80 per cent. Typical gellants used with this system include substituted polystyrenes* and aluminum soaps.*

* Tradenames and manufacturers are listed in Appendix I.

The best wetting agent appears to be glycerol sorbitan laurate* at a concentration of three per cent of the solids weight.

Thus far, the most promising carrier for the solvated type of boron slurry is isopropyl alcohol. With ball-milled commercial-grade boron, stable slurries showing viscosities of less than 200 poise (at 100 sec^{-1}) are available at solids loadings from 70 to about 80 per cent by weight. Thus far, the best wetting agent for these slurries is n-octylamine, present at three per cent of the boron weight.

Ball-milling the boron results in agglomerates of primary particles, which are believed to be welded and/or held together by adhesive impurities on the surface of the primary particles. It is this size distribution (and the associated surface area reduction) which allows desirable rheological properties of the slurries at solids loadings above about 70 per cent.

1.3 OBJECTIVES OF THE PRESENT PROGRAM

The results of the boron slurry fuel development effort performed by Atlantic Research Corporation under Contracts AF 33(616)-7432, AF 33(657)-11260, and AF 33(657)-12290 led to the definition of a number of problem areas requiring investigation.[1,2] Many of these problem areas were studied during the program covered by this report, performed under Contract AF 33(657)-14336.

The primary objectives of this program were to develop promising boron slurry fuels for use in a low-altitude ramjet vehicle, and to evaluate these fuels in terms of physical properties and combustion performance. In order to accomplish these objectives, the following tasks were undertaken:

(1) Development and evaluation of slurry formulations containing ultra-fine boron powders (150 Å to 1,500 Å particle diameters);

(2) Development of methods for economical and nondiscriminatory combustion testing of promising slurries in a sub-scale ramjet engine;

(3) Establishment of a base line for comparison of sub-scale combustion evaluation with other slurry combustion testing;

(4) Definition of the various trade-offs which exist among boron slurry properties, and application of these trade-off functions to slurry evaluation;

(5) Investigation of the effects of temperature on the rheological properties of promising boron slurry formulations.

2.0 FORMULATION AND CHARACTERIZATION

The slurry formulation and characterization studies performed on this program included work in the development of slurries containing ultra-fine boron powders, optimization of promising slurry formulations, thermal characterization of several promising formulations, stability testing, and determination of particle-size distributions in slurries.

2.1 DEVELOPMENT OF SLURRIES CONTAINING ULTRA-FINE BORON

Ultra-fine boron powders were considered potentially useful in enhancing the combustion properties of slurry fuels, due to the small primary particle sizes available (150 Å to 1,500 Å particle diameters). An additional improvement in slurry combustion performance also appears to be available from the use of this type of boron because of the high purity of the powder(up to 99.9 per cent free boron).

2.1.1 Types of Boron

Three types of boron powder, which differ in particle size, purity, and method of manufacture, were used in the program. A summary of the properties of these powders is presented on Table I.

The manufacturers from whom the boron powders were obtained are listed in Appendix I. In this report, ultra-fine boron powder produced by the pyrolysis of diborane will be referred to as "high purity, ultra-fine boron"; ultra-fine boron powder produced by arc reduction of BCl_3 will be referred to as "sub-micron boron"; and boron powder nominally one micron in diameter produced by the thermite reduction of B_2O_3 will be referred to as "commercial-grade boron".

The impurities present in commercial-grade boron include magnesium metal (about 5.5 per cent), oxides of boron and boric acid (about two per cent), water (up to two per cent), and small amounts of various borates and borides. A free boron analysis of commercial-grade boron, as received, usually indicates approximately 90 per cent purity. The small amount of impurity in high purity, ultrafine boron (as received) is hydrogen, but this type of boron powder will rapidly adsorb water from the atmosphere.

TABLE I

PROPERTIES OF THREE TYPES OF BORON POWDERS USED IN SLURRY FUEL DEVELOPMENTAL STUDIES

TYPES OF BORON*	METHOD OF MANUFACTURE	NOMINAL PARTICLE SIZE	FREE BORON CONTENT (per cent)	APPROXIMATE HEATING VALUE (Btu/lb)	VOLUMETRIC HEATING VALUE (Btu/cu ft)
COMMERCIAL-GRADE	THERMITE REDUCTION OF B_2O_3	~ 1u	≈ 90.0	24,200	3.44×10^6
SUBMICRON	ARC REDUCTION OF BCl_3	500 to 1500 Å (0.05 to 0.15 u)	≈ 95.0	24,200	3.48×10^6
HIGH PURITY, ULTRA-FINE	PYROLYSIS OF B_2H_6	100 to 200 Å (0.01 to 0.02u)	99.9	25,500	3.69×10^6

* NAMES OF SUPPLIERS ARE PRESENTED IN APPENDIX I.

A weight increase of about two per cent has been recorded for an exposed sample within two hours, but no further measurable increase in weight occurred (the relative humidity in this test was 50 per cent). The ultra-fine boron powder is produced, packaged, and shipped under an inert atmosphere of nitrogen gas.

Chemical analysis of the sub-micron boron powder (manufactured by arc reduction of boron trichloride) has revealed that this material is about 95 to 96 per cent free boron. The impurities are believed to be mostly boric oxide, boric acid, and water, but a small amount of carbon is also usually present. The submicron material could probably be supplied at a higher purity if the material were protected from contact with air.

2.1.2 Formulation Variables and Properties

The solids loadings which could be attained with as-received boron produced by diborane pyrolysis (high purity, ultra-fine) were about 35 per cent in JP-4 and 50 per cent in isopropanol. Solids loadings for as-received boron formed by BCl_3 reduction in an arc process (submicron) were similar or only slightly higher in the same two carriers. Increasing the bulk density of the ultra-fine boron 50 per cent by shaking 24 hours on a laboratory shaker table allowed solids loadings up to approximately 55 per cent in JP-4 or isopropanol. Slightly greater loadings (up to 61 per cent in JP-4) were obtained with ultra-fine boron which had undergone several hours of laboratory ball-milling. Ball-milling for 67 hours produced a relatively thin slurry at 70 per cent by weight ultra-fine boron. Optimization of this formulation involved variation of the wetting agent concentration to achieve minimum viscosity. This was accomplished by observation only, since an optimum wetting agent-to-boron ratio of 0.06 to 1 was established in work at the 50 per cent solids level. A slurry of 70 per cent solids with a wetting agent-to-boron ratio of 0.04 to 1 was made, but it was extremely viscous in comparison to the first slurry. Higher wetting agent concentrations were also considered, but the resulting slurries were very thick.

Ball-milling of submicron boron for 67 hours resulted in a slightly grainy, but loose slurry at 75 per cent solids. The ratio of wetting agent-to-boron in this case was about 0.064 to 1, which also had been determined as optimum at the 50 per cent solids level. This slurry of 75 per cent submicron boron in JP-4 and the slurry of 70 per cent ultra-fine boron in JP-4 were manufactured in 15-pound lots for use in combustion testing in the micro-ramjet. The formulation data and rheological data for these two slurries are presented in Figure 1.

The boron used in these slurries was ball-milled in a steel laboratory mill for 67 hours. It should be noted that results of chemical analysis of this ball-milled material indicated that several per cent of the boron may be oxidized during the ball-milling operation.

2.1.3 Discussion of Optimized Slurries

Even though no gellant was used in the ultra-fine boron slurries, they have appeared to be very stable in shelf-storage tests up to 21 months. This stability is believed to be the result of the presence of some residual ultra-fine particles and porous agglomerates which interact strongly with each other. In addition, the relatively high wetting-agent concentrations used may enhance particle-carrier interaction to the point of creating a structure capable of supporting the particles. The apparent stability of these slurries does not compromise their desirable viscosity - shear rate relationships. For both slurries the apparent viscosity over a shear rate range of several hundred to several thousand was below 100 poise at ambient conditions. These results compare well with the viscosities which have been achieved for slurries of 80 per cent ball-milled commercial boron in JP-4 and 75 per cent ball-milled commercial boron in isopropanol.

The solids loadings attained in this work (70 per cent for high purity, ultra-fine boron and 75 per cent for submicron boron) appear to be near the upper limits for the ultra-fine particle powders. Some improvement would be expected from extensive ball-milling, which might be prohibitively time-consuming, but no other method of increasing the loadings of the high purity boron is presently known. Some of the slurry formulation

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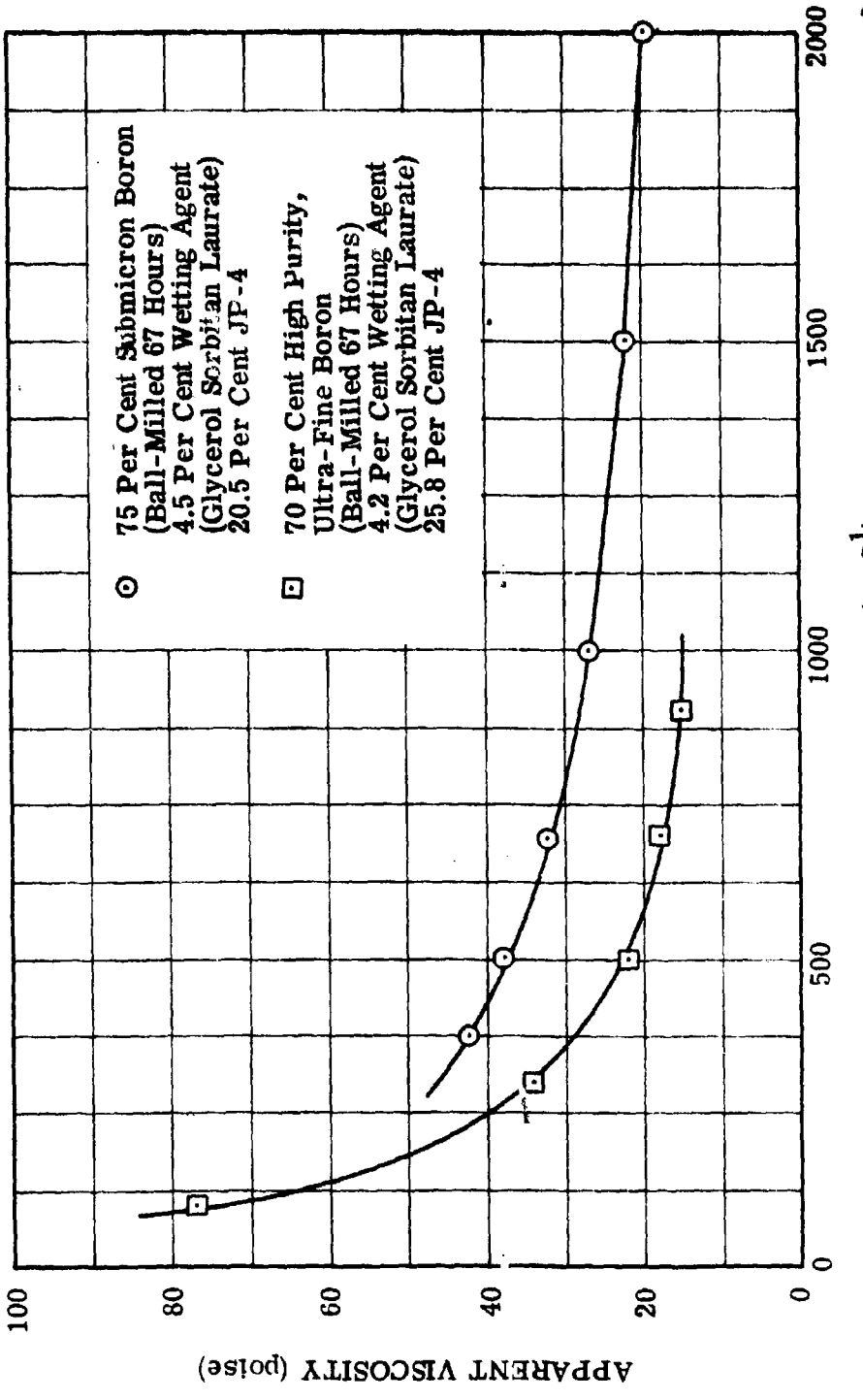

Figure 1. Apparent Viscosity Versus Shear Rate for Final Ultra-Fine Boron Slurry Formulations.

and property determination work with high-purity boron powders, and in particular the earlier work at lower solids loadings, was performed under Contract No. AF 33(657)-11260. More detailed information on the formulation of these slurries and properties of the high-purity boron powders is available in the Final Report for that contract (Reference 1).

2.2 DEVELOPMENT OF 1965 "WORKHORSE" FORMULATION

Slurries of ball-milled boron in the 1964 "workhorse" formulation (73 per cent boron in JP-4 with an aluminum soap gellant) were not stable for more than a few days of storage. Since this formulation was considered a standard one to be used in thermal characteristics studies and other testing, effort was applied toward developing a more stable "workhorse" formulation. The formulation optimization for this slurry was based on the stability under centrifugation, shelf life, and rheological properties. Based on the optimization of 80 per cent slurries performed under Contracts AF 33(657)-11260[1] and AF 33(657)-12290[2], the gelling resin selected was a modified polystyrene and the wetting agent was glycerol sorbitan laurate. The concentration of the wetting agent was fixed at three per cent of the solids weight. Therefore, the concentration of gelling resin in the JP-4 was the only process variable studied. In this study the gellant concentration ranged from zero to six per cent of the carrier weight.

The results of viscosity determinations and the separations (bleeding) resulting from 750 "g's" for 24 hours for the slurry formulations used in the optimization are presented on Table II. The viscosities are compared at 100 sec^{-1} shear rate. More complete rheological data on these and other 73 per cent boron formulations using different gellants and/or wetting agents are available in the Final Report under Contract No. AF 33(657)-11260[1]. The viscosities on Table II were determined by the Severs (extrusion) method, and the per cent separation represents the amount of clear liquid carrier which could be removed by methanol extraction after centrifugation.

The data on Table II indicate an expected increase in apparent viscosity with increasing gellant concentration. The amount of separation,

TABLE II

COMPARISON OF APPARENT VISCOSITY AT 100 SEC^{-1} AND SEPARATION UNDER 750 "G'S" FOR 24 HOURS FOR WORKHORSE FORMULATIONS (73 PER CENT BORON) CONTAINING VARIOUS GELLANT CONCENTRATIONS

NO.	SLURRY FORMULATION		APPARENT VISCOSITY[1] AT 100 SEC^{-1} poise	SEPARATION AT 750 "g's" FOR 24 HOURS[1] per cent
1	Boron (44 hr. ball-milled)	-73.0%	29	8.5
	Wetting Agent[2]	- 2.19%		
	Gellant[3]	- 0.50%		
	JP-4 Carrier	-24.31%		
2	Boron (44 hr. ball-milled)	-73.00%	42	9.0
	Wetting Agent[2]	- 2.19%		
	Gellant[3]	- 0.74%		
	JP-4 Carrier	-24.07%		
3	Boron (44 hr. ball-milled)	-73.0%	59	3.5
	Wetting Agent[2]	- 2.19%		
	Gellant[3]	- 0.99%		
	JP-4 Carrier	-23.82%		
4	Boron (44 hr. ball-milled)	-73.0%	126	1.0
	Wetting Agent[2]	- 2.19%		
	Gellant[3]	- 1.49%		
	JP-4 Carrier	-23.32%		

[1] The "per cent separation" was determined as the weight of clear liquid resulting from centrifugation times 100 divided by the weight of the original sample. Each of the values given is averaged from two test values obtained.

[2] The wetting agent used was glycerol sorbitan laurate

[3] The gellant was a modified polystyrene

(Manufacturers are listed in Appendix I)

however, dropped sharply for Slurry No. 3 (gellant concentration four per cent of carrier) and continued to decrease as the gellant concentration was increased further. On the basis of these results, the formulation designated No. 3 in Table II was chosen as the 1965 "workhorse" formulation for use in systems testing. The apparent viscosity of the finalized formulation was 59 poise at 100 sec^{-1} and 73 poise at 60 sec^{-1} shear rates.

2.3 THERMAL CHARACTERIZATION OF BORON SLURRIES

The temperature range over which boron slurry fuels may be required to operate is -65°F to +300°F. A temperature of -65° represents the lowest ambient temperature (external to the missile) which will normally be encountered, and +300°F represents the expected upper limit of temperature at the interior wall of the fuel tank. As may be expected, stability is the limiting factor at the higher temperatures, and the rheological properties of the slurries comprise the critical operating factor at the lower end of the temperature range. The objective of this portion of the program was to determine detrimental effects of high and low temperature on slurry performance, for the general formulations (at several values of solids loadings) of ball-milled commercial-grade boron in gelled JP-4 or in isopropanol.

2.3.1 High Temperature Stability

The stability of boron slurries under conditions of 300°F and 500 lb/sq.in. pressure for periods up to 24 hours was investigated as a part of the slurry atomization studies (which will be described in detail later). Heating for long periods of time at the above conditions produced no adverse effects in a slurry of 75 per cent ball-milled boron in isopropanol, but a slurry of 73 per cent ball-milled boron in JP-4 formed a hard cake in each of two tests, the first at 390°F and 500 lb/sq.in. for 24 hours, and the second at 310°F and 500 lb/sq.in. for four hours. In the tests with the JP-4 based slurry, however, it appeared possible that an adequate seal had not been obtained, and it was not known whether the observed hardening of that slurry was caused by carrier loss or by polymerization of slurry components.

A differential thermal analysis of the same JP-4 based slurry was performed using a heated, circulating bath of high-temperature silicone oil. Matched thermocouples were placed in the slurry and in the oil. The results of this test, shown on Table III, indicated that no exothermic or endothermic processes occurred within the slurry when heated to about 300°F for over two hours.

After the slurry had been cooled to room temperature its appearance was similar to that before heating; in fact, the slurry appeared slightly looser after being heated. Based on the results of this test and the poppet atomization tests using isopropanol-based slurry, (discussed in detail in Section 3.2) the thermal stability criterion of 400°F for four hours with no detrimental effects appears to be relatively easily attained. The hardening of the JP-4 based slurry during the poppet atomization tests must now be attributed to carrier loss through vaporization, which was permitted by a poor seal in the apparatus.

2.3.2 Effects of Low Temperature

The experimental work described in this section was performed by the University of Dayton (Ohio) Research Institute using slurry samples supplied under this contract. Interpretation of the results in terms of boron slurry stability and rheological requirements for systems applications was the responsibility of Atlantic Research under the present program. Further information, including characterization of the equipment, procedures, and more detailed rheological analysis of the experimental data (including data on other non-Newtonian systems) can be found in unclassified memoranda produced by the University of Dayton Research Institute (References 3,4, and 5).

2.3.2.1 Tests Conducted by UDRI

The two types of viscometers being used by the University of Dayton Research Institute are a rotating viscometer* and a modified version of the Severs extrusion rheometer system (supplied by Atlantic Research). The rotating viscometer used is a concentric cylinder viscometer, in which the

* Trade names and suppliers are listed in Appendix I

TABLE III

BATH AND SAMPLE TEMPERATURE DATA FOR THERMAL STABILITY TEST AND DIFFERENTIAL THERMAL ANALYSIS OF 73 PER CENT BORON-JP-4 SLURRY AT 300°F AND 500 PSIG

ELAPSED TIME hours	BATH TEMPERATURE (T_B) °F	SAMPLE TEMPERATURE (T_S) °F	$\Delta T = (T_B - T_S)$ °F
0.75	230	111	119
1.00	268	131	137
1.25	322	164	158
1.50	345	196	149
1.75	368	248	120
2.00	362	263	99
2.25	348	281	67
2.50	345	295	50
2.75	338	299	39
3.00	340	299	41
3.25	338	300	38
3.50	338	300	38
3.75	332	297	35
4.00	332	297	35
4.25	332	297	35
4.50	337	298	35
4.75	336	298	38
5.00	336	298	38

outer cylinder is stationary and the inner cylinder rotates in the fluid. The temperature of the sample is controlled by a liquid bath about the outer cylinder. This rotating viscometer is more flexible than the capillary viscometer system in that time-dependency of fluid properties as well as approximations of yield stress can be determined quickly. The required sample size of about 50 milliliters is also much smaller than that of the capillary system, which is about 500 milliliters for the typical rheograms determined by Atlantic Research on this program. The rotating viscometer is, however, restricted to rather low shear rates in the case of very viscous slurries because of maximum torque limitations. For thin boron slurries, or at elevated temperatures, shear rates up to 1000 sec^{-1} can be achieved, but for thick slurries (viscosity > 100 poise) the upper limit is about 10 sec^{-1} or less.

Shear stress-shear rate data taken with the rotating and capillary systems by the University of Dayton Research Institute are compared with Atlantic Research capillary data for the same 73 per cent solids, JP-4-based boron slurry on Figure 2. The Atlantic Research correlation was based on the assumption of a power law fluid in the region of shear rate covered. Formulation data for the slurry (UD-6) are presented on Table IV. According to Figure 2, the data from the rotating viscometer are consistent with the capillary data over a limited shear rate range, in this case, 10 to 50 sec^{-1}. The deviation of the two curves at higher shear rates is typical of the comparison tests that were made, and is attributed to the fact that the samples tested in the rotating viscometer are tested in a fully sheared condition, whereas the capillary instrument does not allow sufficient time for the slurry to reach a fully sheared state. Which of the two tests is more representative of a given flow system is determined by the residence time of the slurry in the system. For a very long residence-time transfer through a pipe, of course, the rotating viscometer (fully sheared) data would be expected to apply more closely than the capillary results.

Some rotating viscometer points were taken with the UD-6 slurry

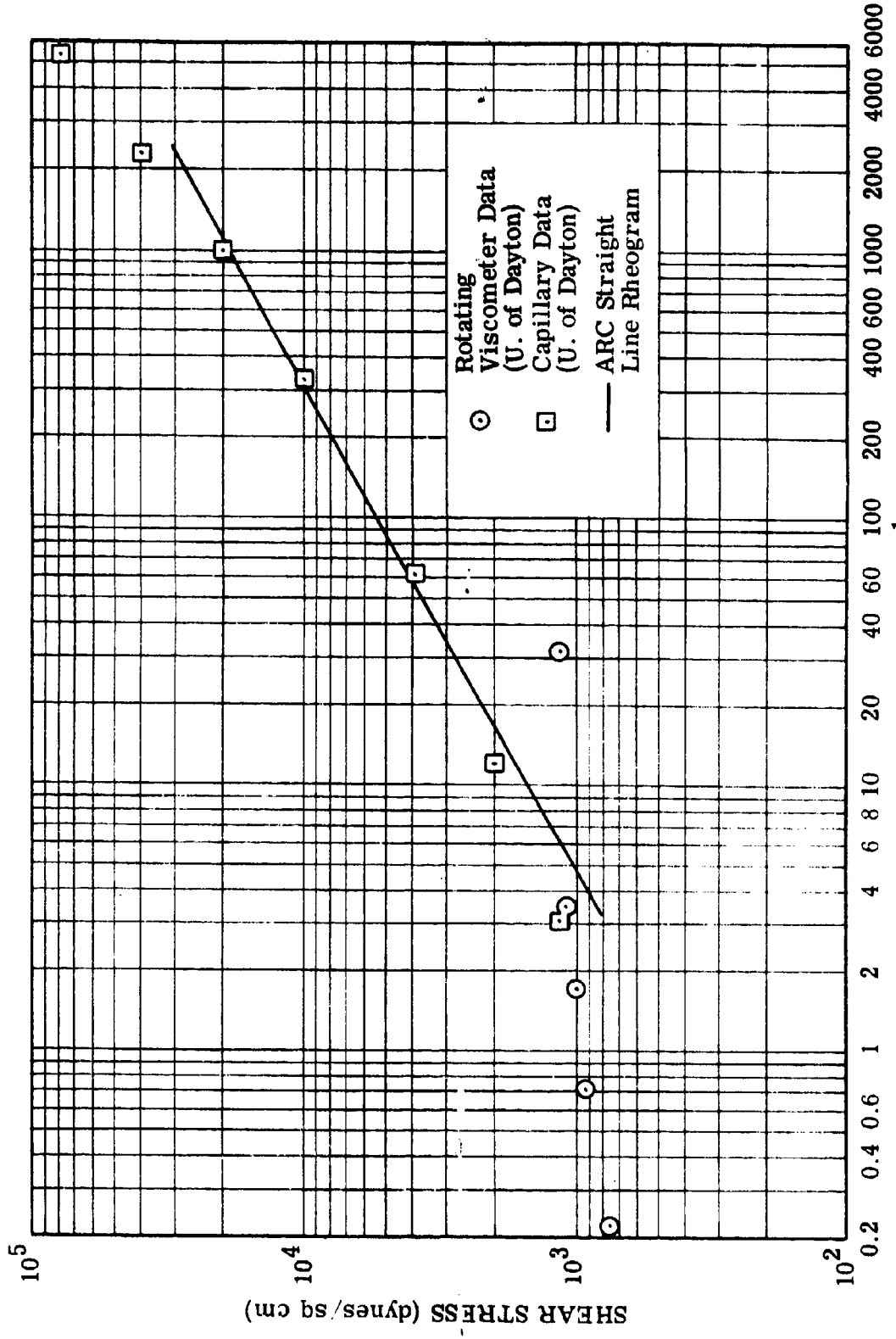

Figure 2. Shear Stress - Shear Rate Data for Boron Slurry UD-6 (Formulation Data on Table IV). Temperature 68°F.

TABLE IV

APPARENT VISCOSITIES AT -65°F and 100 sec^{-1} SHEAR RATE FOR SLURRY FORMULATIONS USED IN RHEOLOGICAL STUDIES AT THE UNIVERSITY OF DAYTON RESEARCH INSTITUTE

Code No.	Formulation		Gellant Concentration Per Cent of Carrier	Apparent Viscosity at -65°F and 100 sec^{-1} Shear Rate Poise
UD-6	Boron (64-hr. Ball-milled)	73.00%	4	5,350
	JP-4	23.82%		
	Gellant (Modified Polystyrene)[1]	0.99%		
	Wetting Agent (Glycerol Sorbitan Laurate)	2.19%		
		100.00%		
WH-10	Boron (64-hr. Ball-milled)	73.00%	3	90
	JP-4	24.06%		
	Gellant	0.75%		
	Wetting Agent	2.19%		
		100.00%		
WH-13	Boron (64-hr Ball-milled)	73.00%	2	550
	JP-4	24.31%		
	Gellant	0.50%		
	Wetting Agent	2.19%		
		100.00%		
WH-14	Boron (64-hr. Ball-milled)	73.00%	0	170
	JP-4	24.81%		
	Wetting Agent	2.19%		
		100.00%		

[1] The same gellant and wetting agent were used for all of the slurries(except WH-14, in which no gellant was used).

at shear rates less than 0.1 sec^{-1}, but these low shear rates are believed to be beyond the limit of accuracy for the apparatus. The data as shown indicates that the magnitude of the yield stress of the UD-6 slurry at room temperature is approximately 10^3 dynes/sq. cm. (2 lb/sq.ft.).

2.3.2.2 System Considerations in Rheological Measurements

In general, boron slurries are pseudo-plastic materials which also exhibit time-dependent and viscoelastic properties. The studies at Dayton University with the rotating viscometer have indicated that times of the order of one second may be required for a flowing slurry to reach a fully sheared condition in a duct; therefore, the apparent viscosity which can be applied to a slurry in a transfer line would most likely fall somewhere between the values obtained from relatively short rheometer tubes (partially sheared state) and from the rotary instrument (fully sheared state), unless the L/D ratio of the line were extremely large. It would be helpful to determine residence times necessary for attainment of the fully sheared state in a tube, which can be accomplished through the use of a range of capillary L/D ratios. Another potential problem area involves the use of a high-shear pump for pumping slurry, in which case the slurry flowing downstream of the pump might be fully sheared or sheared beyond the normal fully sheared state. In the latter case, the pressure drop (or apparent viscosity) would be less than that predicted by rotating viscometer data taken at the fully sheared condition, unless rapid slurry separation resulted from the shearing action of the pump.

2.3.2.3 Effects of Temperature on Boron Slurry Rheology

The effect of temperature on the shear stress - shear rate plot for the UD-6 slurry (formulation on Table IV) is presented on Figure 3. As expected, the shear stress for a given shear rate increases as the temperature is lowered. The effect of gellant concentration (modified polystyrene gellant) on apparent viscosity at various shear rates over the temperature range of -65°F to +80°F for slurries of 73 per cent ball-milled boron in JP-4 is presented in Reference 3. The formulation and apparent viscosity

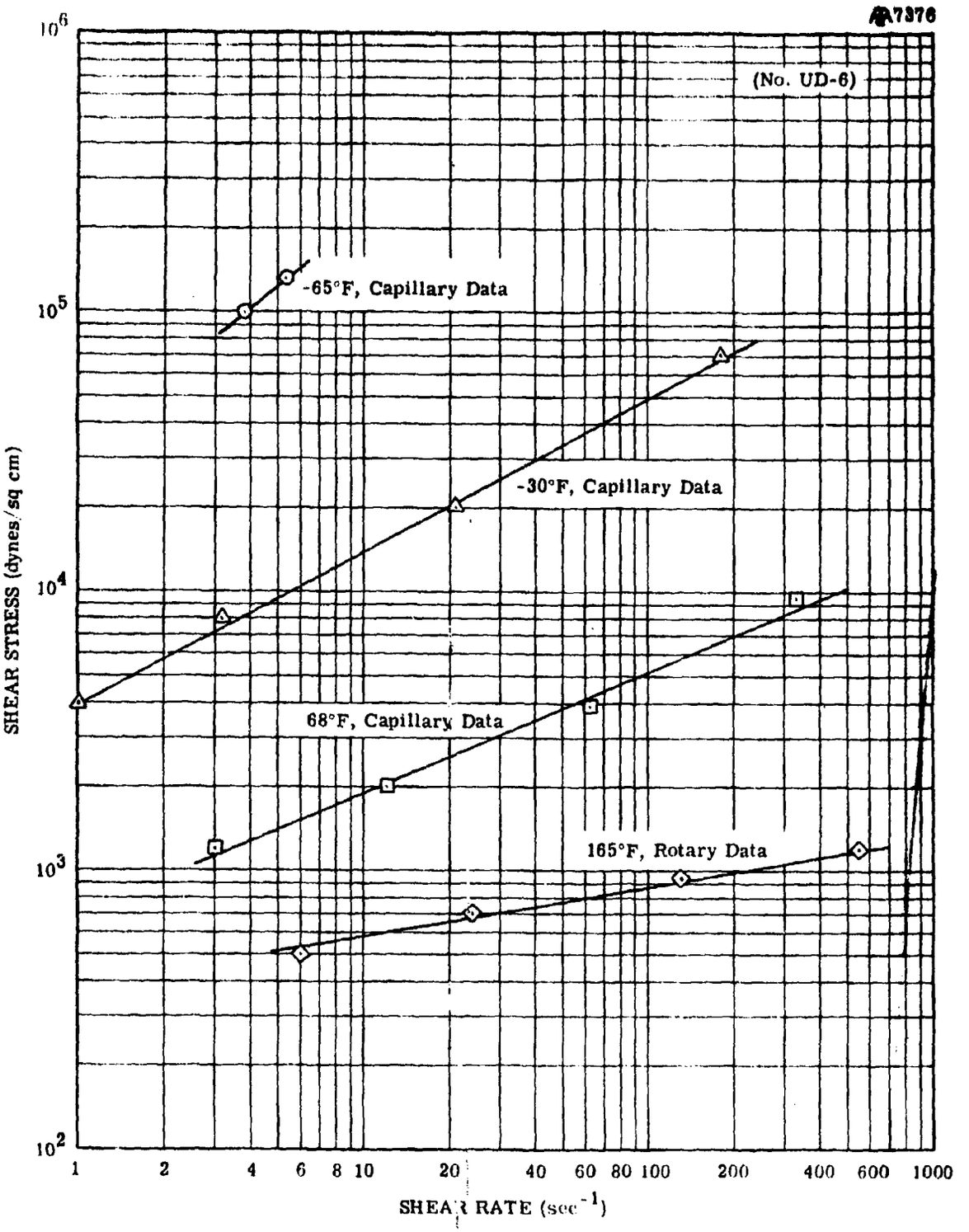

Figure 3. Effect of Temperature on the Shear Stress - Shear Rate Relationship for a Slurry of 73 Per Cent Ball-Milled Boron in JP-4.

data at 100 sec^{-1} shear rate and -65°F for these slurries are also presented in Table IV. The slurry containing a gellant concentration of three per cent of the carrier phase (WH-10) produced apparent viscosities lower than any of the other three slurries, including the sample containing no gellant.

If the data for WH-10 are excluded, a consistent plot of apparent viscosity (at 100 sec^{-1}) versus gellant concentration at a given temperature within the range can be made (for example, Figure 4). For the -65°F condition, the plot on Figure 4 indicates that a gellant concentration of about 1.5 per cent of the carrier will result in a viscosity of 400 poise at a shear rate of 100 sec^{-1}.

2.3.2.4 Effect of Solids Loading and Carrier

Another series of tests was performed to determine the effect of solids loading on slurry viscosity at low temperatures. The formulation data for these tests are presented in Table V. Isopropanol and gelled JP-4 were used as carriers, and the solids loadings were 75 and 80 weight per cent for the isopropanol-based slurries and 50, 73, 80, and 85 weight per cent for the JP-4 based slurries. Values of apparent viscosity for these slurries at a shear rate of 100 sec^{-1} and at temperatures of -30°F and -65°F are also presented in Table V. The experiments from which these data were obtained were performed by the University of Dayton Research Institute using the extrusion rheometer.

According to the data in Table V, the use of isopropanol as a slurry carrier, instead of JP-4, resulted in no significant difference in values of apparent viscosity at low temperatures. An apparent difference was noted between the viscosities of samples UD-6 and UD-4 at -30°F, but the general trends of the data cast doubt on the low value at -30°F for slurry UD-6 (73 per cent boron in gelled JP-4).

Although most of the data points in Table V were obtained from extrapolation across an order of magnitude of shear rate, the relative increases in viscosity as solids loading was increased are consistent with trends observed for similar slurries at ambient temperature[2].

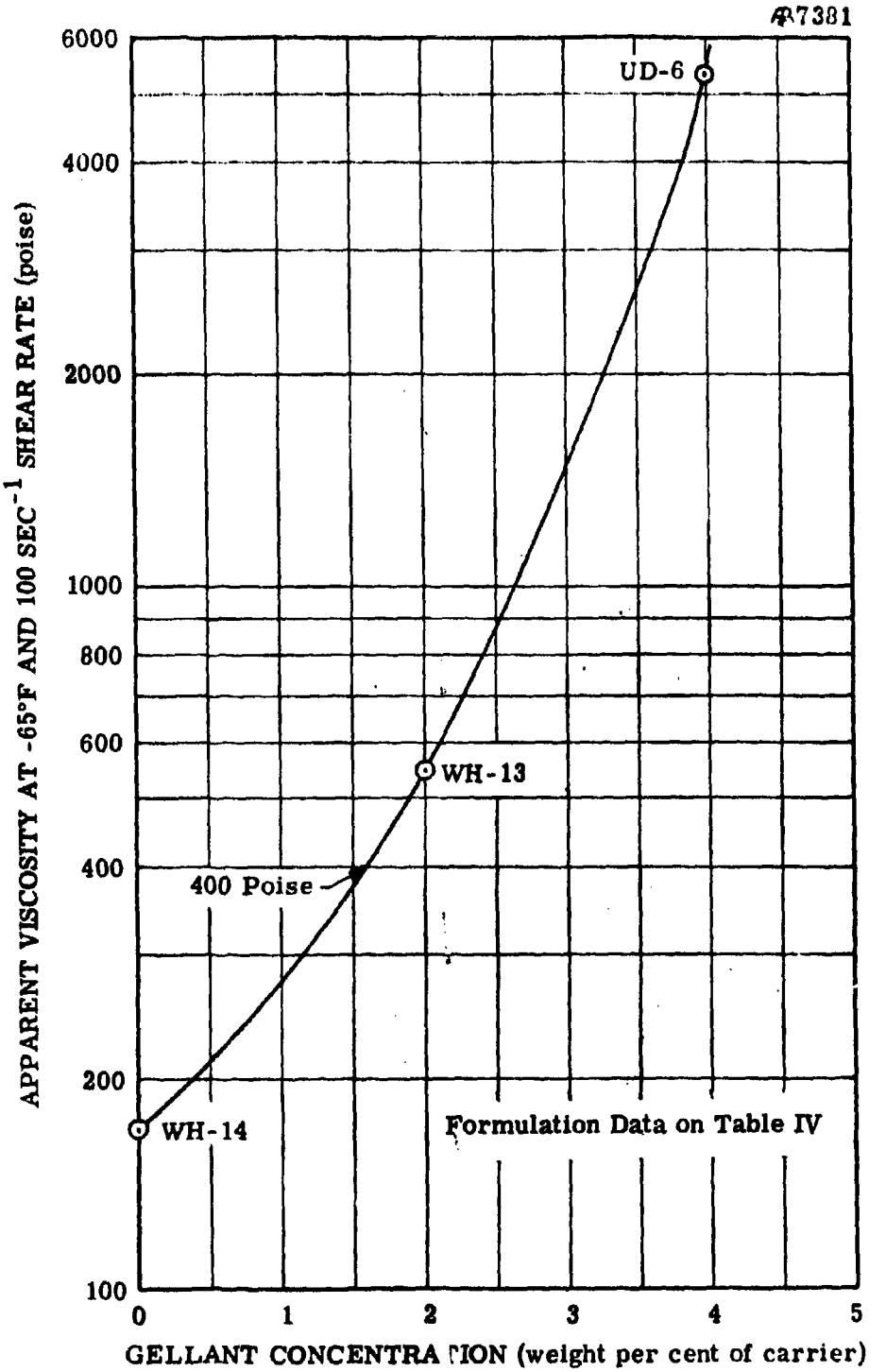

Figure 4. Effect of Modified Polystyrene Gellant Concentration on Apparent Viscosity of a 73 Per Cent Boron JP-4 Slurry at -65°F.

TABLE V

EFFECTS OF SOLIDS LOADING ON THE APPARENT VISCOSITY AT LOW TEMPERATURES OF SEVERAL TYPES OF BORON SLURRY FORMULATIONS, BASED ON DATA GENERATED BY UNIVERSITY OF DAYTON RESEARCH INSTITUTE USING A CAPILLARY (Extrusion-Type) RHEOMETER
(All Boron was Commercial Grade, Ball-Milled 44 hours)

SLURRY SAMPLE NUMBER	FORMULATION	APPARENT VISCOSITY ($100\ sec^{-1}$, poise) At -30°F	At -65°F
UD-4	75.00 PER CENT BALL-MILLED BORON 1.88 PER CENT n-OCTYL AMINE 23.12 PER CENT ISOPROPANOL	1410	4200
UD-5	80.00 PER CENT BALL-MILLED BORON 2.40 PER CENT n-OCTYL AMINE 17.60 PER CENT ISOPROPANOL	11,200	-
UD-12	50.00 PER CENT BALL-MILLED BORON 1.94 PER CENT GELLANT[a] 1.50 PER CENT WETTING AGENT[b] 46.56 PER CENT JP-4	760[c]	1800
UD-6	73.00 PER CENT BALL-MILLED BORON 0.99 PER CENT GELLANT[a] 2.19 PER CENT WETTING AGENT[b] 23.82 PER CENT JP-4	450	5350
UD-7	80.00 PER CENT BALL-MILLED BORON 0.70 PER CENT GELLANT[a] 2.40 PER CENT WETTING AGENT[b] 16.90 PER CENT JP-4	10,500	
UD-8	85.00 PER CENT BALL-MILLED BORON 0.50 PER CENT GELLANT[a] 2.55 PER CENT WETTING AGENT[b] 11.95 PER CENT JP-4	VISCOSITIES TOO HIGH TO MEASURE	

a. THE GELLANT USED WAS A MODIFIED POLYSTYRENE.

b. THE WETTING AGENT USED IN THE JP-4 BASED FORMULATIONS WAS GLYCEROL SORBITAN LAURATE.

c. THIS TEST WAS MADE AT -35°.

2.3.2.5 Discussion of Low-Temperature Effects on Viscosity.

At -65°F, the apparent viscosities at a shear rate of 100 sec^{-1} (for promising types of boron slurries optimized in terms of minimum viscosity and maximum storage stability at ambient temperature) are approximately 5,000 poise. This resistance to flow is beyond the capability of many types of fuel delivery systems, including the centrifugal pumps presently planned for use with the boron slurry fuels. Therefore, it is recommended that methods of reducing the viscosity of boron slurries at low temperatures, without compromising other properties (stability, combustion performance, etc.) be investigated.

An apparent viscosity of about 500 poise at 100 sec^{-1} appears to be a practicable maximum value for a slurry that is to be pumped centrifugally. Perhaps this desired tenfold decrease can be effected by altering formulation variables, through improved methods of boron processing, or by slightly decreasing the solids loadings. From a comparison of the data on Figure 4 with the data at -65°F on Table V, it is obvious that, for the JP-4 based system, apparent viscosity at low temperature is a much stronger function of gellant concentration than of solids loading. Therefore, the use of improved gellants, which can provide storage stability at low gellant concentrations, appear to be a strong possibility for reducing viscosity at low temperatures for this type of slurry.

2.3.3 Effect of Temperature on Yield Stress

Estimations of yield stress for boron slurries at various temperatures were obtained by extrapolation of the University of Dayton data, from extrusion rheometer tests, to a shear rate of one sec^{-1}. This method is considered valid only for an order of magnitude approximation of yield stress, and the values obtained are believed to be conservative on the high side. The estimated yield stress values are presented in Table VI. It is obvious from these data that temperature has a strong effect on the yield stress of boron slurries. The yield stress of isopropanol-based slurries appears to be higher than those for the JP-4 based slurries.

TABLE VI

ESTIMATION OF YIELD STRESS VALUES AT VARIOUS
TEMPERATURES FOR TWO BORON SLURRY FORMULATIONS
(VALUES OBTAINED FROM EXTRAPOLATION OF UNIVERSITY OF DAYTON
RESEARCH INSTITUTE CAPILLARY VISCOMETER DATA TO ONE SEC^{-1} SHEAR RATE)

Temperature °F	Estimated Yield Stress, lb/sq ft. 73% Boron in JP-4 (1965 Workhorse)	75% Boron in Isopropanol
+165	1	--
Ambient	2	4
+32	--	10
Zero	3	30
-30	8	50
-65	105	200

TABLE VI

ESTIMATION OF YIELD STRESS VALUES AT VARIOUS TEMPERATURES FOR TWO BORON SLURRY FORMULATIONS (VALUES OBTAINED FROM EXTRAPOLATION OF UNIVERSITY OF DAYTON RESEARCH INSTITUTE CAPILLARY VISCOMETER DATA TO ONE SEC^{-1} SHEAR RATE)

Temperature °F	Estimated Yield Stress, lb/sq ft. 73% Boron in JP-4 (1965 Workhorse)	75% Boron in Isopropanol
+165	1	--
Ambient	2	4
+32	--	10
Zero	3	30
-30	8	50
-65	105	200

Yield stress, which may be described as the force per unit area necessary to initiate shear (or flow), becomes important in fuel-system startup, especially for a system of large L/D having a fairly small value of pressure drop available. According to Marquardt engineers, a high yield stress could create startup problems in the bladder feed system presently under consideration for use in LASRM-type missiles because of a "coring", or blow-through, effect in the bladder. This results in an effective bladder L/D of about 30 and requires that, for the present bladder design, yield stress be not higher than about 12 lb/sq. ft. According to Table VI, this requirement would severely limit the use of the present slurries at low temperatures.

Two methods are available for solving this problem, and perhaps a combination of both methods would result in elimination of the difficulty. First, the bladder tank can be designed to reduce the coring effect. One method of accomplishing this may be to provide a tapered connection from the bladder to the fuel line. Second, gellants may be available which will allow reductions in yield stress at low temperature, and/or other formulation variables can be optimized to reduce yield stress (for instance, elimination of water in the slurries).

Some progress appears to have been made on the second method of reducing yield stress. Recent yield stress data generated by the University of Dayton Research Institute on slurries made with a promising "aluminum salt"* gellant are presented in Table VII. Although these data were obtained with the rotating viscometer, they should be at least as valid as those obtained by the extrapolation method and presented in Table VI. The very low values for the three per cent gel case are probably misleading, but the remainder of the data indicate that yield stresses below 12 lb/sq. ft. at -65°F may be available with this gellant. However, it should be mentioned that these formulations have not been investigated in terms of storage, stability or viscosity at -65°F and 100 sec^{-1} shear rate.

* Manufacturers are listed in Appendix I.

TABLE VII

EFFECT OF TEMPERATURE ON YIELD STRESS
OF BORON SLURRIES CONTAINING "ALUMINUM SALT"
GELLANT (BASIC FORMULATION - 73% BALL-MILLED BORON IN JP-4)

Temperature	Yield Stress, lb/sq ft.				
	0.5%	1.0%	3.0%	4.0%	6.0%
°F	Gel[1]	Gel[1]	Gel[1]	Gel[1]	Gel[1]
Ambient	---	0.05	0.45	1.05	1.42
+32	---	0.11	0.40	1.25	3.77
Zero	---	0.16	0.55	1.32	4.47
-30	0.40	1.24	0.82	1.42	3.39
-65	28.9	6.15	1.82	9.51	38.0

[1]The gellant concentration is expressed as the percentage of the carrier (liquid plus gellant) weight, not as a percentage of the total formulation weight.

2.4 SLURRY STABILITY TESTING

The present requirement for slurry storage stability specifies that there be no phase separation in two years of shelf storage. For the formulations presently under study, this requirement appears to be well within their capability. In fact, a formulation which has not exhibited "bleeding" (syneresis) after about three months of shelf storage will not separate on indefinite storage. However, storage stability is thus far compromised for slurries which exhibit low viscosities at -65°F, and slurries optimized for low temperature rheology may necessarily possess marginal storage stability characteristics.

2.4.1 General Results to Date

There are three modes of storage instability in boron slurries, as follows:

(1) Phase separation (syneresis or "bleeding")

(2) Increased viscosity (and yield stress)

(3) Gas formation resulting in decreased bulk density

For hydrocarbon-based slurries phase separation has been controlled mainly by the gellant type or concentration used. Other variables, including wetting agent type and concentration, and the method of boron processing used, also affect storage stability, but it has proved advantageous to optimize these variables on some basis other than storage stability. For instance, a "standard" ball-milling time of 44 hours has been established on the basis of the most efficient operation (loading and unloading the mill) to obtain ball-milling times over 36 hours.

For isopropanol-based slurries, phase separation is controlled primarily by solids loading, although ball-milling time and wetting agent concentration both have some effect. In general the isopropanol-based slurries are more stable on a batch-to-batch basis than the hydrocarbon-based slurries; in other words, for a given hydrocarbon-based slurry optimized on the basis of minimum viscosity and maximum stability, there

is a high probability that some batches will not be stable to phase separation, whereas for the solvated slurries there is a low probability of batch-to-batch nonreproducibility. This occurs probably because of the more complex nature of the chemical interactions which occur in the gelled systems as compared to the more simple solvated system. This relative simplicity of the isopropanol-based slurries also accounts for the absence of viscosity changes during storage for these slurries. In the gelled system the strength of the gel structure is strongly dependent on the amount of wetting agent present in the liquid phase. Most of the wetting agent migrates to the boron surface during mixing, but the high porosity of the boron allows it to slowly adsorb more wetting agent during storage, which, in turn, allows the gel structure to strengthen. Viscosity increases up to about 200 per cent have been observed with gelled systems as shown on Figure 5. The yield stress of hydrocarbon-based slurries also increases during storage, probably through the mechanisms described above.

Gas formation and the resulting increase in pressure and reduction in bulk density is very important from a systems standpoint. Bulk density reductions of 25 per cent for a hydrocarbon-based slurry and 9 per cent for an isopropanol-based slurry have been measured in previous work[2]. Obviously, a density reduction of this magnitude would negate the potential advantage in volumetric heating value offered by boron slurry fuels; therefore, the elimination of gas formation in boron slurries appears to be a most important problem.

The gas formed in the hydrocarbon-based slurries is hydrogen, and the mechanism of formation is believed to involve chemical reaction of water (or hydroxyl groups) present on the surface of the boron with the boron (or possibly with some impurity such as magnesium). Gas formation can probably be eliminated through removal of surface water, either through vacuum drying, hydrogen reduction of the surface, or by washing in isopropanol.

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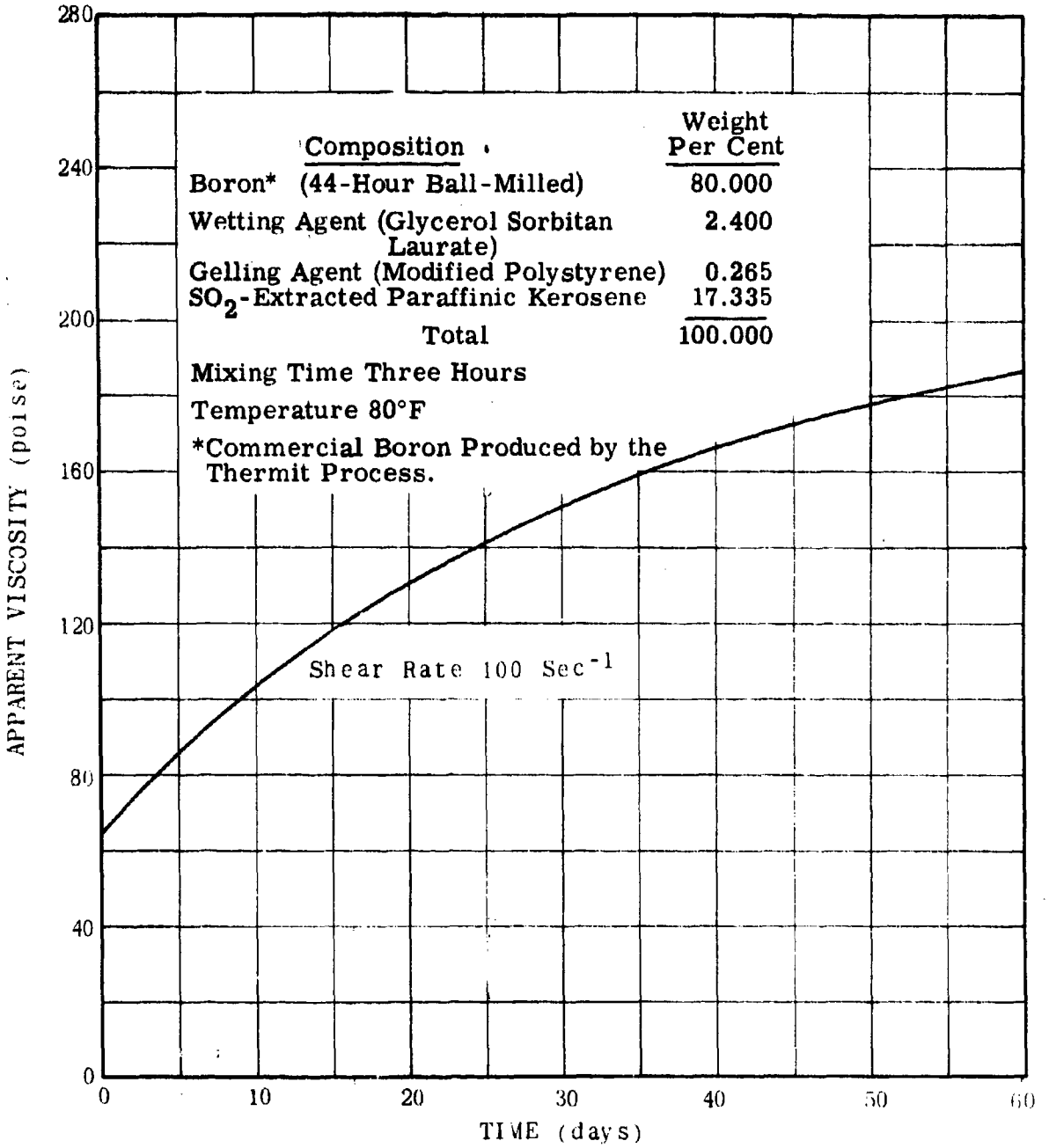

Figure 5. Viscosity of 80 Per Cent Boron Slurry as a Function of Time at 80°F.

2.4.2 Stability to Vibration

Two samples of the 1965 workhorse formulation formulation (73 per cent ball-milled, commercial-grade boron in gelled JP-4) were vibrated at low frequency to test stability to separation under vibration. The specific conditions used were 50 cycles per second for seven hours at 5 "g" and at 10 "g". Neither sample exhibited any phase separation, but significant rheological changes were found. The apparent viscosity and yield stress were found to be increased by a factor of about three as a result of the vibration tests, as shown on Figure 6. This increase is attributed to accelerated aging (normally, increase in viscosity with storage time) resulting from the vibration.

2.4.3 Correlation of Storage Stability with Stability to Centrifugation

Storage of the slurry samples manufactured during the optimization work on the 1965 workhorse formulation (see Table II) resulted in the correlation between stability to separation during storage (at ambient temperature), and phase separation during centrifugation, shown on Table VIII. Based on these data, a slurry formulation which exhibits less than four or five per cent separation (weight of clear liquid produced divided by total weight of sample, expressed as a percentage) during centrifugation at 750 "g" for 24 hours will not separate in storage at room temperature.

2.4.4 Correlation of Storage Stability with Yield Stress

The magnitude of the yield stress of a boron slurry may also be a measure of its storage stability. Of six batches of "1965 workhorse" slurry (73 per cent boron in JP-4 gelled with four per cent of the carrier weight of modified polystyrene gellant) supplied to the Marquardt Corporation, one separated slightly on storage. The yield stress of the batch which showed separation (Batch I) was the lowest of all the batches, as shown on Table IX. These results indicate that, for the workhorse slurry, a yield stress of about two lb/sq.ft. may be necessary to prevent separation. For slurry fuel systems presently under consideration a maximum yield stress of 12 to 15 lb/sq ft is considered acceptable.

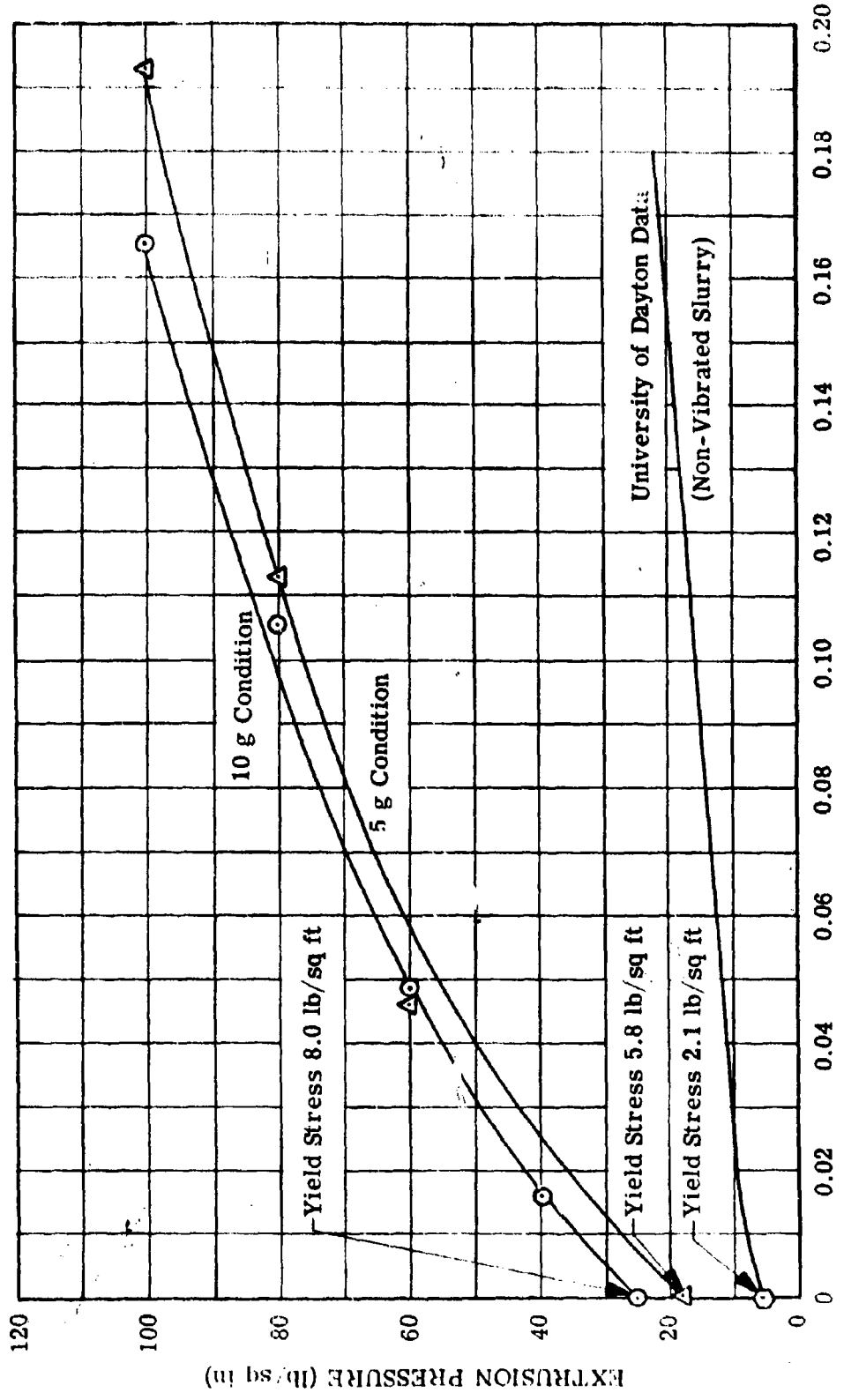

Figure 6. Results of Extrusion Rheometry (Single Tube) of 1965 Workhorse Boron Slurry Vibrated 8 Hours at 50 cps and 5 g or 10 g Accelerations.

TABLE VIII

RESULTS OF STORAGE AND CENTRIFUGATION FOR SLURRIES
OF 73 PER CENT BALL-MILLED BORON IN JP-4
CONTAINING VARYING AMOUNTS OF MODIFIED POLYSTYRENE GELLANT
(FORMULATION DATA ON TABLE II)

Slurry No.	Gellant Content Per Cent of Carrier	Storage Time to Observable Separation	Separation in Centrifuge at 750g for 24 Hours (Per Cent of Sample Weight)
MH-11	6	No separation after 200 Days	1.0
UD-6	4	No separation after 200 Days	3.5
SH-10	3	60-80 Days	9.0
MH-13	2	60-80 Days	8.5
MH-14	0	3-4 Days	8.5

TABLE IX

RELATION OF YIELD STRESS[a] OF THE 1965 "WORKHORSE" BORON SLURRY[b] TO STORAGE AND TRANSPORT STABILITY

Batch No.	Yield Stress at 70°F Lb/Sq.Ft.	Remarks on Stability
I	1.03	Separated slightly on transport and storage
II	2.23	No separation
III	4.39	No separation
V	2.50	No separation
VI	3.43	No separation

[a] Testing performed with a rotating viscometer by the University of Dayton Research Institute.

[b] Formulation as follows:

Ball-Milled Commercial Boron	73.00%
JP-4 Carrier	23.82%
Modified Polystyrene Gellant	0.99%
Glycerol Sorbitan Laurate (Wetting Agent)	2.19%
	100.00%

2.4.5 Effect of Container Geometry on Stability to Separation

The stability of hydrocarbon-based slurries to separation also appears to depend on the size of the storage container; or, specifically, on the diameter, in the case of a cylindrical storage vessel. In various storage experiments over the past three years it has been noted that, in a number of instances, slurries which do not separate when stored in glass jars about two inches in diameter will separate rapidly when stored in jars which are about four inches in diameter. This phenomenon, which does not appear to apply in the case of isopropanol-based slurries, may involve a critical diameter for storage containers which is determined by some characteristic, such as the chain length, of the gellant. The problem of a critical diameter becomes especially significant in the case of shipment and/or storage of slurries in large drums.

2.5 DEVELOPMENT OF ISOPROPANOL-WASHED BORON SLURRY

As a general rule, slurries of solid particles in liquids can be loaded to higher solids loadings (or, conversely, will produce lower viscosities at a constant solids loading) when a distribution of particle sizes is used. There are exceptions, however, which can be attributed to irregularity of particle shapes, particle porosity, or the use of extremely fine particles. In most of these exceptions high viscosity is believed to be caused by the large surface areas and the subsequent large amounts of adsorption of the carrier (or surfactant, in some cases) resulting from the properties mentioned above.

Desirable blending of particle sizes might include particle diameters in a ratio of from five to ten, and in a ratio of about five to ten parts of the larger particles to one part of the smaller particles for a typical bimodal distribution. Such a distribution appeared to be possible with washed commercial grade boron (~1 micron in diameter) and the submicron boron (about 1,000 Å or 0.1 micron in diameter). The carrier used was isopropanol, and the overall objective of the test was to increase the solids loading of a washed boron slurry in isopropanol above the 65 per cent leval attainable with washed commercial boron alone.

The commercial boron used had been ball-milled 44 hours and washed several times in boiling isopropanol for removal of surface contamination prior to mixing with the submicron sample. The ratio used was about 6 parts commercial boron to one part ball-milled sub-micron boron. The mixture was made to about 40 per cent solids by adding isopropanol. This thin slurry was then boiled for an hour, allowed to cool and settle, and the clear liquid was decanted off. This washing procedure was repeated once. The produce was placed in a mixer and mixed without sealing the mixer. Thus, the carrier could slowly escape during the mixing operation. Solids loadings were determined about once a day. At solids loadings of 46 and 52 per cent the slurry was very fluid. The slurry began to thicken considerably at a solids loading of 67.5 per cent, which was taken to be the maximum solids loading for the formulation. This result may represent a slight increase in attainable solids loading through the addition of submicron boron, but the difference is not significant in terms of theoretical volumetric heat release.

The next test of this formulation included the use of n-octyl amine as a wetting agent at a concentration of three per cent of the boron weight. The procedure of the test included addition of the wetting agent to the mixture containing 67.5 per cent solids, followed by mixing in an unsealed mixer heated by a hot water jacket until the slurry dried up into hard spheres. Then isopropanol was added at intervals until thick, but wet, slurry was produced. The solids loading at this point (considered the maximum for the formulation) was 78.8 per cent, or about 17 per cent higher than that of the mixture containing no wetting agent.

More isopropanol was added in order to reach a solids loading of 75 per cent, for comparison with other slurries at this solids loading. The actual solids loading after dilution was 74.3 per cent. (In this test the attainment of exactly 75 per cent solids would have been very difficult since the total weight of slurry could not be determined.) It should be noted here that the residual dried material resulting from the solids loading determinations was tested for amine content contributed by the wetting agent. Since no amine was found by spectroscopic analysis,

it can be assumed that the solids loadings are correct as stated.

A plot of apparent viscosity versus shear rate for the resulting slurry (at 74.3 per cent solids) is presented on Figure 7. According to Figure 7, the slurry was strongly pseudo-plastic and showed no indication of dilatant behavior up to a shear rate of 10,000 sec^{-1}. The final slurry was very smooth and was similar in appearance to isopropanol-based slurries containing ball-milled boron.

This type of simple slurry may prove very desirable in terms of storage stability, rheological properties, and (possible) combustion efficiency. Thus far, it appears that the solids loading limit may be around 80 per cent, which could prove to be sufficient to compete with gelled slurries since hydrocarbon-based slurries at 80 per cent solids tend to become dilatant at the higher shear rates. Viscosity of the "simple" formulations containing several types of washed boron may be far from optimized, since several variables (size distribution, wetting agent type and concentration) are involved. We believe that this is one of the most promising formulations yet developed, and that further work should be done to investigate its rheological optimization and combustion characteristics.

2.6 BORON SURFACE CHEMISTRY EXPERIMENTS

The boron surface chemistry work performed on this program included determinations of surface areas of the various types of boron powders used in the work on combustion and formulation and determinations of boron surface reactivity with various adsorbates which might clarify the large differences in chemical reactivity observed in combustion tests with various slurries. Surface area work was performed on high-purity, ultra-fine boron powders, commercial-grade boron powders, and processed boron powders under this contract. The remainder of the surface chemistry studies were directed toward definition of the impurities on the surface of the boron and their effects on combustion of atomized slurries of various types. A detailed account of the techniques and apparatus used in the boron surface chemistry work during 1964 and 1965 under Contract

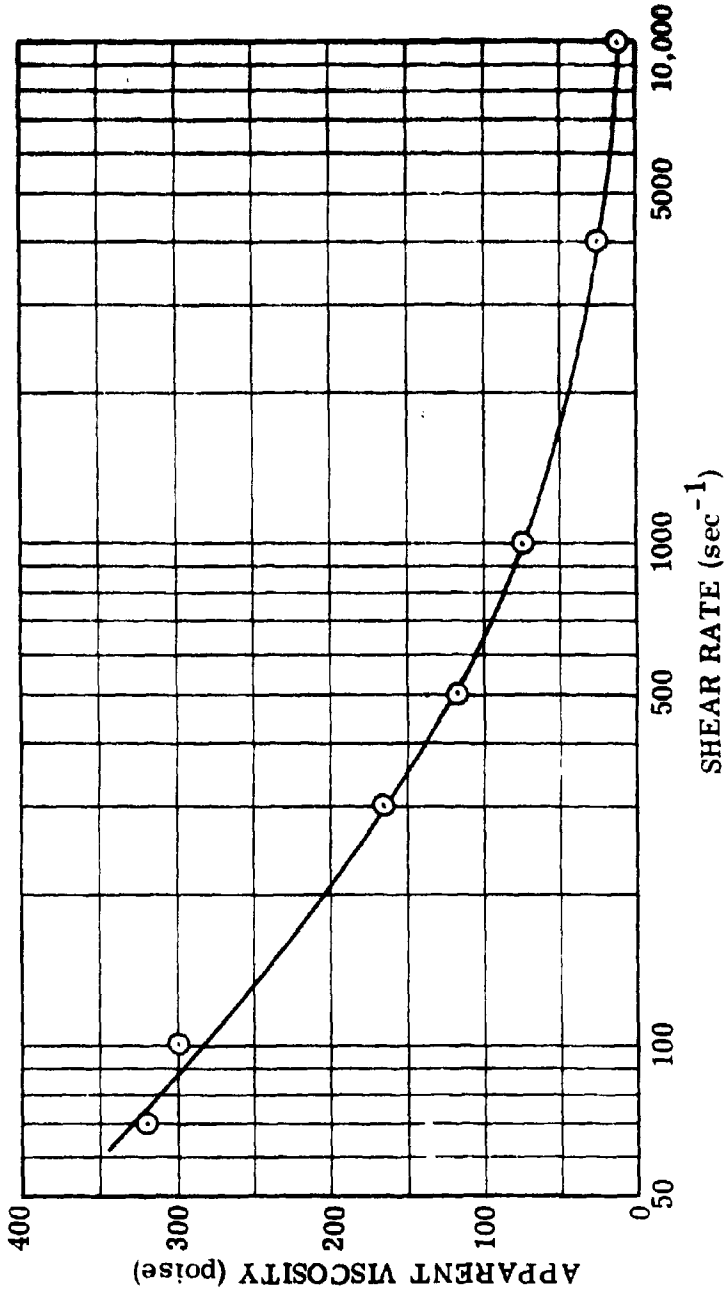

Figure 7. Apparent Viscosity Versus Shear Rate for a Slurry of 74.3 Per Cent Washed Boron (Six Parts Commercial Grade, One Part Avco Ultra-Fine) in Isopropanol (the Wetting Agent, Armeen 8D, was Present at 2.23 Per Cent Concentration).

No. AF 33(657)-11260, and during 1965 under this program, may be found in Reference 6. The same report includes correlations between observed boron surface phenomena and slurry storage and rheological properties.

2.6.1 Surface Areas of Ultra-Fine Boron Powders

The surface area of the submicron boron (produced by BCl_3 reduction) was determined by the B.E.T. technique (Reference 6) to be about 55 sq m/gm, as compared to 17.7 sq m/gm for commercial boron (90-92 per cent pure) and about 135 sq m/gm for ultra-pure boron made from the pyrolysis of diborane. Very little effect of degassing temperature on surface area was observed for the submicron boron. The results of these tests are summarized on Table X.

2.6.2 Methanol Isotherms with Ultra-Fine Boron

The following values were obtained for methanol adsorption isotherms on submicron boron over the range of activation temperature specified:

Activation Temperature °C	Methanol Uptake to Monolayer Coverage, cu cm/sq m
25	0.183
160	0.151
318	0.187
318	0.203

These values and the shape of the plot of methanol uptake versus activation temperature for submicron boron powder are consistent with the data for both high-purity, ultra-fine boron and commercial-grade boron reported elsewhere[1]. The reduction in methanol uptake between 25°C and 160°C activation temperature indicates a surface change between these temperatures, strongly suggesting that some surface contamination is present. For the submicron boron, this was borne out by a series of chemical analyses which indicated a free boron content of 95 to 97 per cent, or somewhat below the nominal 99 per cent level.

2.6.3 Reduction Surface Area of High-Purity, Ultra-Fine Boron

Surface areas of processed and unprocessed high-purity, ultra-

TABLE X

COMPARISON OF SURFACE AREAS OF THREE TYPES OF BORON POWDERS (AREAS DETERMINED BY B.E.T. TECHNIQUE)(6)

Type of Boron	Nominal Diameter	Per Cent	Outgassing Temperature °C	B.E.T. Surface Area sq m/gm
Commercial	0.7-1.0μ	90-92	25	17.7
High-Purity, Ultra-Fine (Formed by Pyrolysis of Diborane)	80-160A°	99.9	25	135
Submicron (Formed by Arc Reduction of BCl_3)	300-500A° (3×10^{-2} to 5×10^{-2} μ)	96	25	54.7
Submicron	"	"	160	55.8
Submicron	"	"	318	56.6

fine boron were determined by the B.E.T. technique. The results shown on Table XI, indicate that ball-milling is a better method of compacting this boron powder than washing and vacuum drying. This material emerged from the vacuum oven as a very fluffy, loosely agglomerated powder which returned to the fine powder state under the slightest agitation.

2.6.4 Methanol Adsorption Test Results with Commercial Boron

It has been demonstrated[2] that slurries containing boron which has been washed in a solvent to remove the normal surface contaminants are more active chemically for combustion at ambient pressure conditions than slurries containing as-received or ball-milled boron powder. A study was made to determine the extent and, if possible, the basis of this enhanced reactivity. Methanol vapor was absorbed onto the surface of commercial boron after various treatments (washing, ball-milling, etc.) and following a range of sample activation temperatures at a pressure of 10^{-6} torr.

The general results of these tests are shown on Figure 8. Ball-milled boron, which is typified by the 44-hour milled material, shows a greater over-all reactivity with methanol vapor than washed boron (whether milled before washing or not). The unwashed material also showed a large increase in methanol adsorption per unit area at an activation temperature of 100°C. These results indicate that the over-all reactivity of boron with methanol is reduced by the washing process, instead of being enhanced as was predicted. The increase in reactivity of the unwashed material at 100°F activation is attributed to removal of some surface contamination at 100°C and 10^{-6} torr which was not volatile at 25°C and 10^{-6} torr.

The amount of methanol chemisorbed onto the boron samples is probably more of an indication of their chemical activity. Chemisorption data corresponding to the total adsorption data on Figure 8 are presented on Table XII. It is significant that the ball-milled boron did not chemisorb methanol prior to being either heated to an activation temperature of 100°C or washed and vacuum dried. In either case, removal of contaminants enhanced the chemisorption of methanol. Another parameter which is important

TABLE XI

SURFACE AREA MEASUREMENTS BY B.E.T. TECHNIQUE
FOR PROCESSED HIGH-PURITY, ULTRA-FINE BORON POWDER
(FORMED BY PYROLYSIS OF DIBORANE)

Test No.	Processing	Surface Area sq m/gm
1	None (As received)	130.6
2	Water-Washed and Vacuum Dried	90.3
3	Dry Ball-Milled Approx. Four Hours	87.2

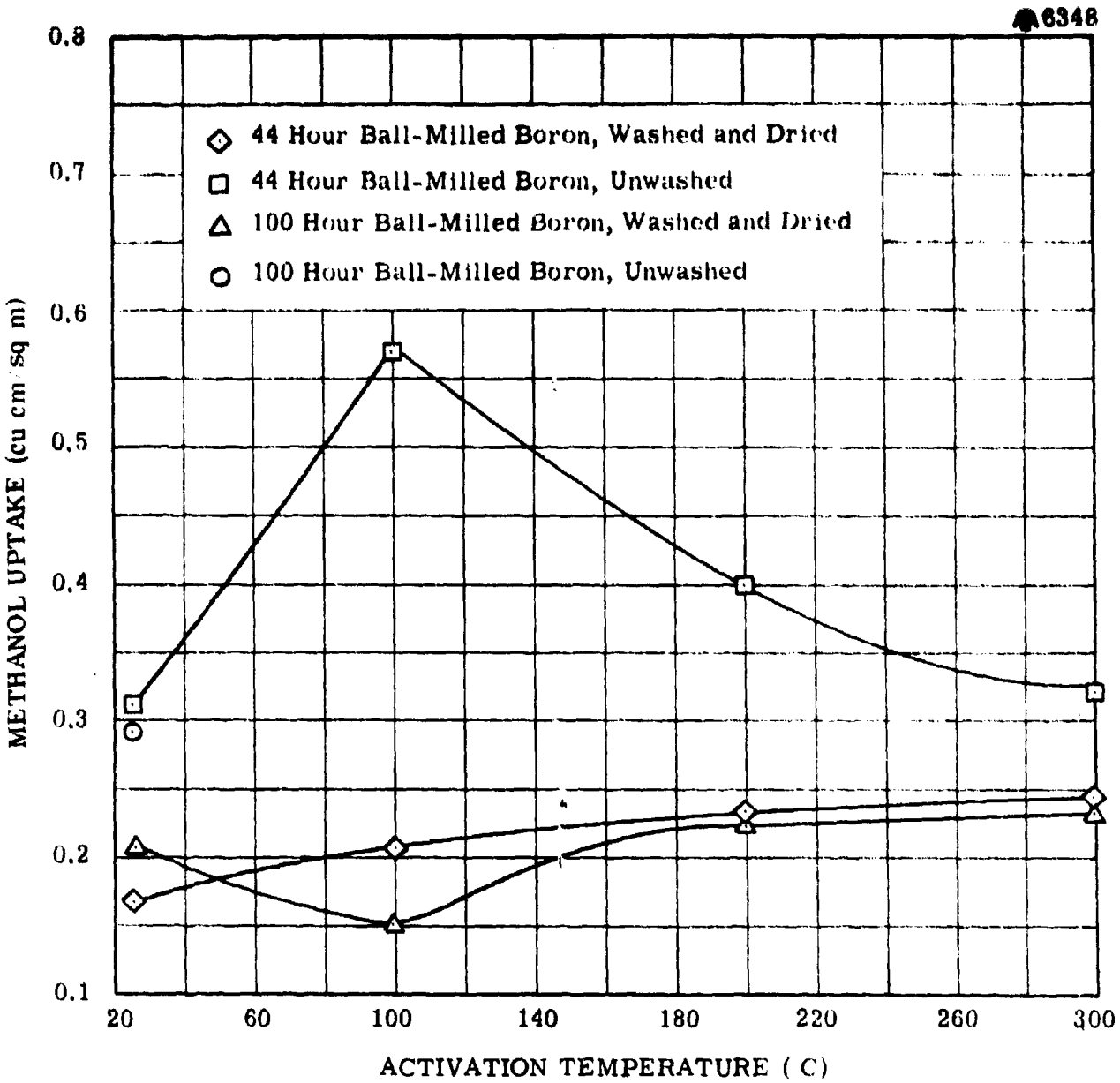

Figure 8. Methanol Uptake Versus Activation Temperature for Ball-Milled Commercial Boron Before and After Washing in Water and Vacuum Drying.

TABLE XII

METHANOL ADSORPTION ISOTHERMS AND SURFACE AREA DATA FOR BALL-MILLED COMMERCIAL BORON BEFORE AND AFTER WASHING IN WATER AND VACUUM DRYING

Sample	Ball-Milling (Time, (Hr.)	Water-Washed	Activation Temperature, (°C)	Methanol Uptake (cu.cm./sq.m.)	Surface Areas (sq.m./gm.)	Methanol Chemisorbed (cu.cm./sq.m.)
1	44	No	25	0.31	9.6	0
2	44	No	100	0.571	10.2*	0.26
3	44	No	200	0.40	11.5	0.22
4	44	No	300	0.32	12.4	0.19
5	44	Yes	25	0.17	14.0	0.04
6	44	Yes	100	0.20	16.0	0.08
7	44	Yes	200	0.25	17.7	0.14
8	44	Yes	300	0.24	18.5	0.16
9	100	No	25	0.29	6.4*	0
10	100	No	100	-	6.3	-
11	100	No	200	-	8.9	-
12	100	No	300	-	8.5	-
13	100	Yes	25	0.21	13.6	0.04
14	100	Yes	100	0.15	14.6	0.07
15	100	Yes	218	0.22	15.7	0.15
16	100	Yes	300	0.23	17.2	0.15

* Average of two points.

to combustion of solid particles, the effective surface area, is also presented for the same samples on Table XII. The surface area data for these samples indicate that the surface areas of the washed samples was greater than that of the unwashed samples throughout the range of activation temperatures.

If it is assumed that the chemical activity is proportional to the number of active sites per gram of boron, then the activities of washed and unwashed, ball-milled boron can be compared on a relative basis, as shown on Table XIII. The relative value of active sites per gram was determined as the amount of methanol chemisorbed per square meter of surface area times the effective surface area in square meters per gram. According to Table XIII, the number of active sites available per gram on the washed boron was equal to or greater than those for the unwashed sample except after 100°C activation.

These results indicate that surface activity of boron can be enhanced by removal of impurities, whether by vaporization of surface contaminants or by removal through solvent extraction. The magnitude of the activity enhancement in these studies becomes significant when compared to a value of zero chemisorption of methanol for the ball-milled sample (unwashed) activated at 25°C and 10^{-6} torr.

In the slurry combustion work performed to date the results of activity enhancement through boron surface improvement alone have been observed in only two cases, both as results of ambient pressure combustor tests[2], as follows :

(1) It has been observed that washed boron in isopropanol carrier (50 per cent solids, no wetting agent) is more active than as-received boron in isopropanol of a similar formulation.

(2) The use of isopropanol, which is a solvent for oxidized boron, as a carrier for ball-milled boron instead of JP-4 results in enhanced chemical activities for similar solids loadings.

TABLE XIII

COMPARISON OF CHEMICAL ACTIVITY OF WASHED AND UNWASHED SAMPLES OF COMMERCIAL BORON IN TERMS OF METHANOL CHEMISORBED (ASSUMED PROPORTIONAL TO THE NUMBER OF ACTIVE SITES) PER GRAM OF SAMPLE (BORON BALL-MILLED 44 HOURS, WASHED IN WATER OR UNWASHED)

ACTIVATION TEMPERATURE, °C	METHANOL CHEMISORBED*, CU.CM./GM.	
	UNWASHED SAMPLE	WASHED SAMPLE
25	0	0.6
100	2.6	1.3
200	2.5	2.5
300	2.4	3.0

*It is assumed that the number of active sites available is proportional to the amount of methanol chemisorbed per gram.

The results of other comparisons of washed versus unwashed boron, such as results of micro-ramjet engine tests described later, may also depend on surface conditioning. In these tests, however, the results obtained also depend on atomization efficiency, carrier volatility, etc., so that the effects of surface treatment are much more obscured than in the direct comparisons mentioned above.

The present interpretation of the numerical values on Table XIII is as follows:

(1) The impurities on the surface of the unwashed boron are mostly boric acid and other compounds involving chemically bound water. As the temperature is elevated, some of these compounds are vaporized away and those remaining are decomposed to water vapor and boric oxide (B_2O_3) which remains on the surface. Since boric oxide is essentially non-volatile and stable, the surface activity does not change further as the temperature is increased.

(2) The impurities on the surface of the washed samples may be a series of boric oxides and borates, some of which are either vaporized or decomposed at each succeeding increase in activation temperatures. Thus, the surface reactivity is increased as more and more boron is exposed through removal of contaminants.

2.6.5 Other Surface Chemistry Work

2.6.5.1 Treatment with Reducing Atmosphere

Ball-milled commercial boron powder was treated by hydrogen gas at 350°C in order to determine if surface properties could be enhanced by hydrogen reduction of contaminants. Exposure to hydrogen was accomplished in a heated, continuous flow reactor, the effluent gas from which was stripped of volatilized material by a liquid nitrogen trap. Significant quantities of boric acid and water were collected in the trap at the

beginning of each run.

The resulting reduced boron powder showed a very low surface area (5.6 sq.m./gm.), but the removal of surface contaminants resulted in relatively high methanol uptakes on an area basis. Chemisorption was also noted after 25°C activation. The product of chemisorbed methanol per unit area times surface area produced results very similar to those presented on Table XIII for washed boron.

The reduced material could not be made into a successful slurry without further treatment because of extensive agglomeration. The presence of agglomeration also indicates that much of the contamination remained (probably as B_2O_3) after the reduction procedure.

2.6.5.2 Catalytic Activity of Boron

It has been reported previously that heating boron onto which methanol has been adsorbed produces a variety of gases, such as methane, ethane, ethanol, propane, and hydrogen. The reduction of methanol by boron contaminated with oxide thus appears likely. In order to determine the extent of such catalytic activity, nitrous oxide was exposed to ball-milled boron (which had been activated at 100°C) at 350°C for 30 minutes. The vapor phase was then collected and analyzed with a mass spectrometer. The analysis indicated that mostly hydrogen was present, but no oxygen or nitrous oxide. The catalytic activity of the boron for N_2O reduction was thus established, but no explanation can be given for the evolution of hydrogen. Hydrogen appears to be generally present in a bound state (perhaps as borane groups) in most of the boron used presently.

2.6.5.3 Reaction of Boron with Oxygen

One test of oxygen adsorption by boron was performed. A sample of water-washed boron (which had been ball-milled 44 hours prior to washing) was activated at 500°C for 22 hours. Hydrogen outgassing of this sample persisted for twenty hours, after which the pressure of 10^{-6} torr was attained. The boron sample was then cooled to 25°C and oxygen gas was

admitted to the system. Adsorption was extremely rapid at first, but, as the pressure was increased, soon reached a constant value. The total amount of adsorption was fairly small, indicating that only a fraction of the surface was covered. However, the very high initial rate of adsorption indicates that there is strong interaction of boron with oxygen at room temperature. From the relatively small amount adsorbed it appears that the reaction of boron with oxygen at low temperatures may involve selective sites.

2.7 PARTICLE SIZE DISTRIBUTION IN BORON SLURRIES

Analyses of particle (agglomerate) size distribution were performed for three boron slurries. The analyses were conducted using an organic solvent with the Coulter Counter instead of saline water. The organic solvent, a mixture of butanol and benzene made conductive with NH_4 CNS, does not dissolve oxidized boron; thus, there is minimal danger of altering the agglomerate particle size during the analysis through removal of adhesive material.

The results of these analyses, shown on Figure 9, indicate that the over-all size distributions for slurries containing ball-milled commercial boron are similar, with a size range of 5 to about 50 microns. There appear to be more smaller particles in the isopropanol-based slurry, probably because the alcohol is a solvent for oxidized boron. The slurry of ball-milled submicron boron appears to contain larger particles than the other two formulations. In fact, about 20 per cent of the boron in this slurry was present as particles larger than 55 microns in diameter. These agglomerates were undoubtedly formed during the ball-milling procedure, but no explanation as to why they were larger than those formed with commercial-grade boron is available.

The size distribution results are consistent with visual observations of the slurries; both slurries of commercial boron exhibited a very smooth consistency, whereas the slurry with ball-milled submicron boron powder was relatively coarse and grainy in appearance.

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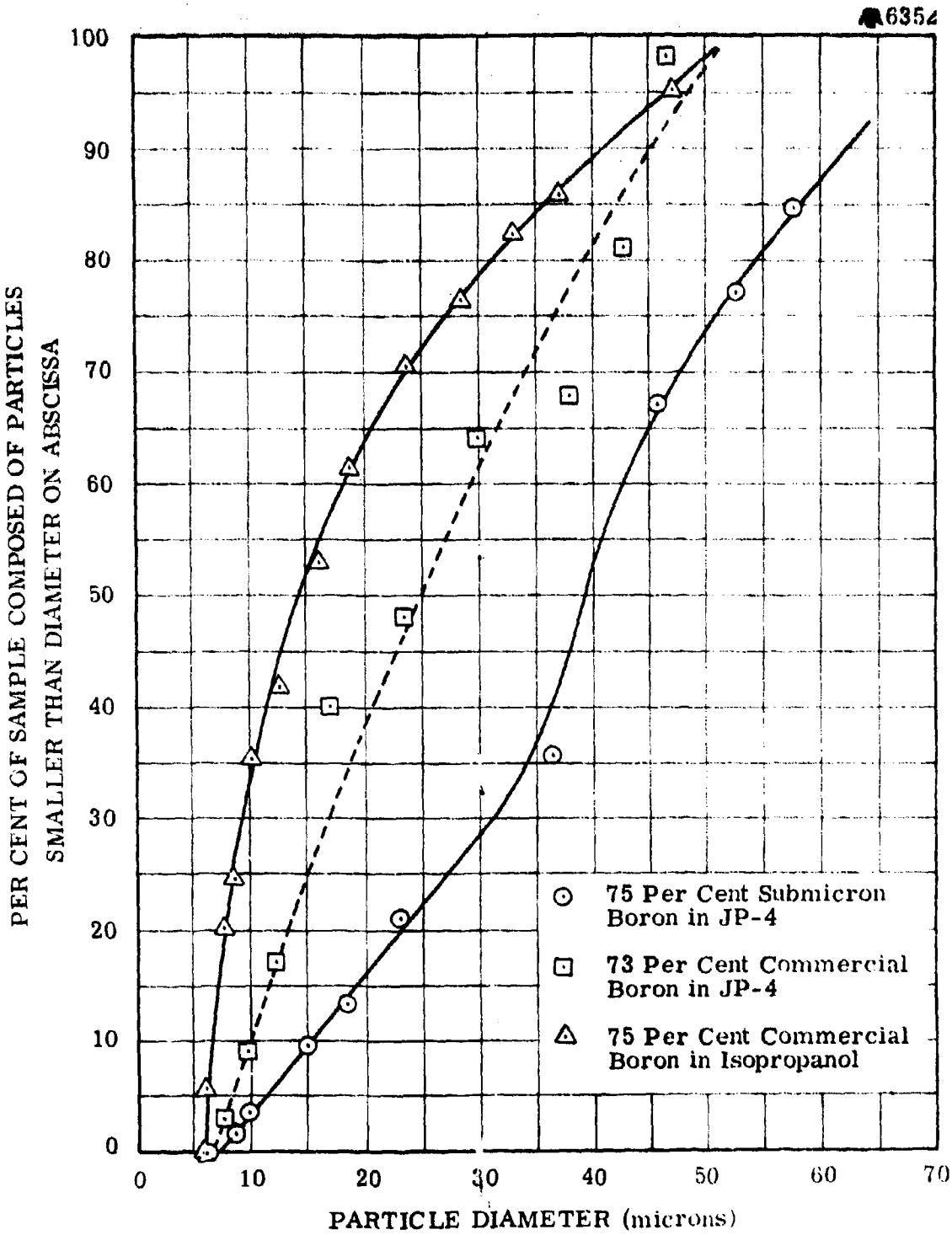


Figure 9. Comparison of Coulter Counter Analyses of Three Slurry Fuel Formulations Containing Agglomerates Resulting from Dry Ball Milling of Boron Powders.

3.0 INVESTIGATION OF SLURRY ATOMIZATION METHODS

Slurry atomization methods were investigated for two reasons: (1) to determine the effects of rheological properties on slurry atomization; and (2) to develop a method of evaluating the combustion properties of experimental slurries that is minimally dependent on their rheological and other properties (including solids loading and carrier volatility). It is considered likely that while particle-mill injection may be satisfactory for some types of boron slurries, such as JP-4-based slurries, it may not be satisfactory for other types, such as isopropanol-based slurries. The particle mill action may be strongly dependent on the rheological properties of slurry during carrier removal, and it appears to be desirable to remove this factor from the combustion evaluation of various slurries as potential ramjet fuels.

In the atomization tests, slurries in both gelled JP-4 and isopropanol were used. These slurries are believed to be representative of the two general types of slurry fuels (non-solvated, as in gelled JP-4, and solvated, as in isopropanol) presently under consideration. The solids loadings in all the tests were 73 per cent in JP-4 and 75 per cent in isopropanol.

3.1 PARTICLE MILL TESTS

Isopropanol-based slurries at 75 weight per cent solids do not atomize well in the particle mill. This is believed due to their rheological behavior which causes smearing of the slurry along the walls of the mill. The smearing results from the high shear rates at the point of injection. As a result of slurry buildup along the walls of the mill, the mill becomes clogged and very little atomization takes place. Large clumps of slurry have been observed to pass through the exhaust nozzle when isopropanol slurry is burned.

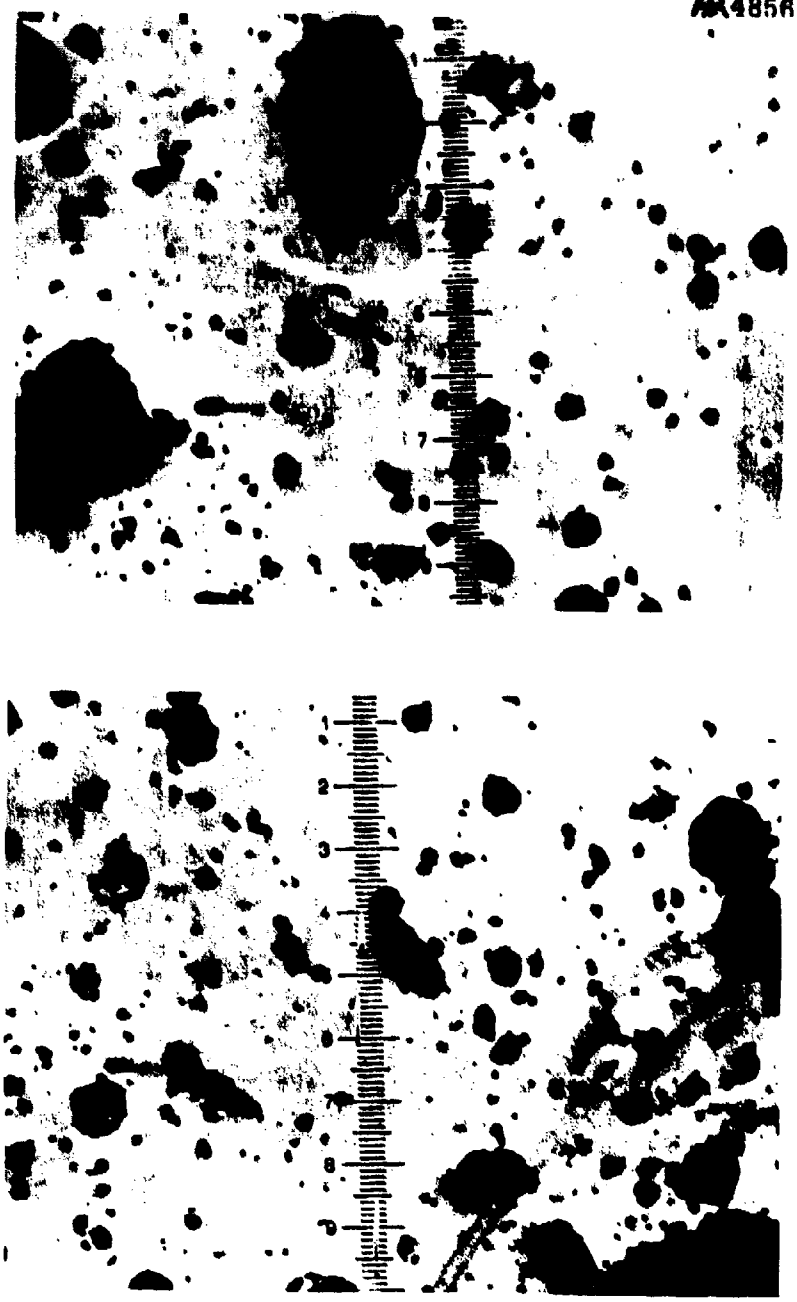
Slurries in which JP-4 is the carrier appear to perform well in the particle mill. A flow test with 600°F air at a fuel-to-air ratio of

1.0 resulted in a spray of fine particles over an exit cone angle of about 15 degrees. As shown on Figure 10, most of the boron that was collected on a greased slide three feet from the outlet was in the form of particles in the size range from 25 to 150 microns in diameter. The largest particles collected in this test were about five thousand microns in diameter. The largest particles on Figure 10 appear somewhat spherical, and this was more noticeable in a sample which impinged on an absorbent paper sheet. These larger particles were wet on impact, as demonstrated by Figures 11, 12, and 13, through comparison with control samples of wet slurry and dry boron forcibly impinged on paper sheets. It is believed that the smaller particles were dry, since only particles above fifty microns in diameter would adhere to dry paper.

High speed motion pictures of the particle mill test with JP-4 slurry revealed that the distribution pattern of particles emerging from the mill was completely annular in shape; that is, there were no particles emerging from the center two inches (approximate diameter) of the three-inch diameter exit. This was expected because of the rotational moment applied to the fuel by the particle mill air, and the expected result is particle impingement on the wall of the burner can prior to ignition. In previous micro-ramjet tests, evidence of this impingement was observed in the form of a buildup of dried slurry on the wall of the burner can one-half to one inch downstream of the particle mill exit.

3.2 POPPET ATOMIZER TESTS

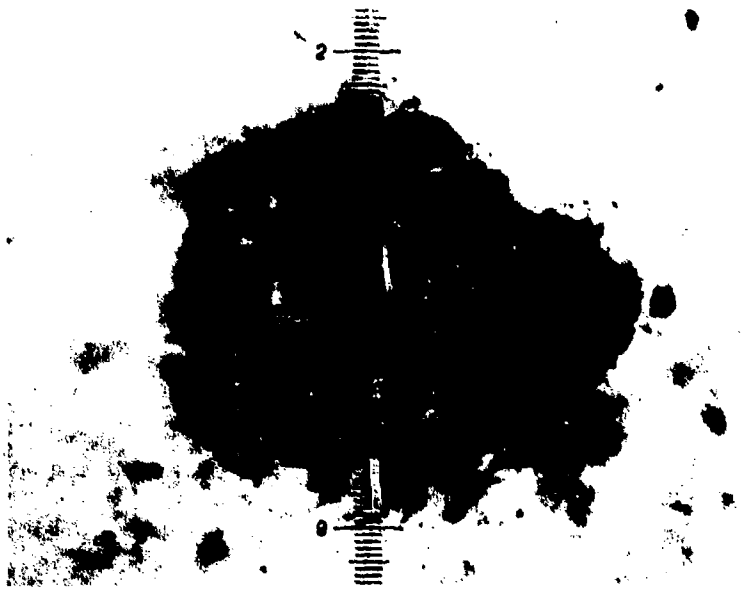
A poppet valve nozzle was constructed and mounted on a small, gas-driven slurry ram. The assembly is shown on Figure 14, and a closeup of the poppet is shown on Figure 15. The turnwheel on the rear of the poppet head was used to adjust the poppet opening. Tests were made with slurry at room temperature and 500 psig pressure and at about 300°F and 500 psig pressure. It was anticipated that the most effective atomization would occur with heated slurry since the carrier would be above or near its boiling point when the slurry issued from the nozzle.



Each Small Division Equals 4.9 Microns

Figure 10. Photomicrographs of Atomized Boron Slurry (73 Per Cent Solids in JP-4) Collected, After Breakup by Particle Mill (Air Temperature 600°F, Air Flow Rate 0.2 lb/sec, Slurry Flow Rate 0.2 lb/sec), on a Greased Slide.

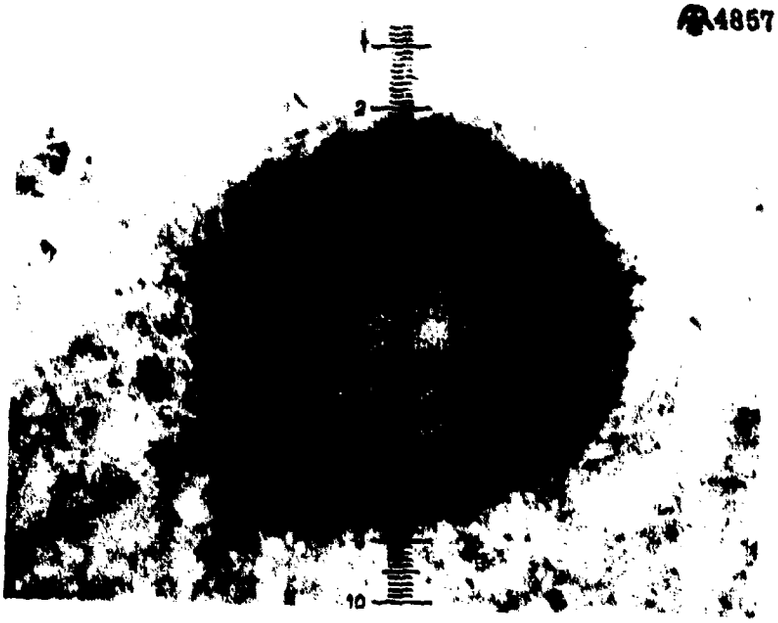
Before Removal of Slurry Bead



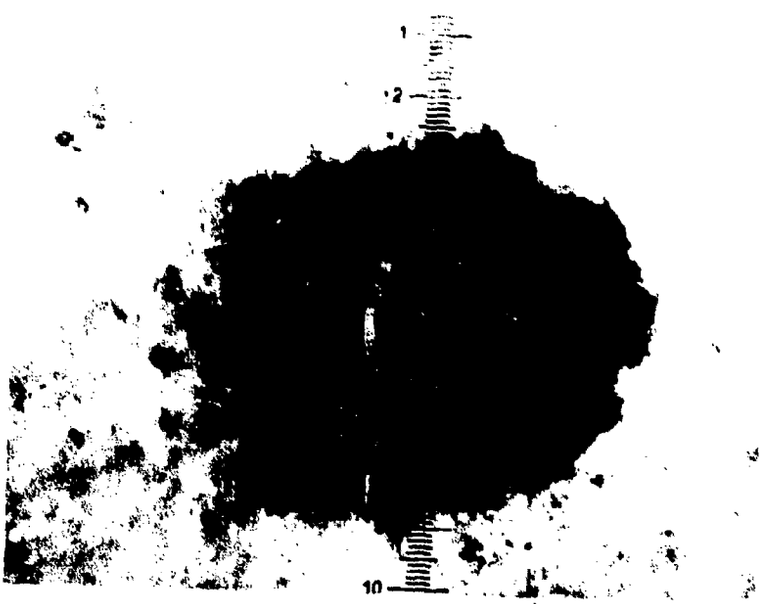
After Removal of Slurry Bead

Figure 11. Photomicrographs of Large Atomized Slurry Particle from Particle Mill Collected on Dry Paper (Slurry of 73 Per Cent Boron in JP-4).

Each Small Scale Division Equals 4.9 Microns



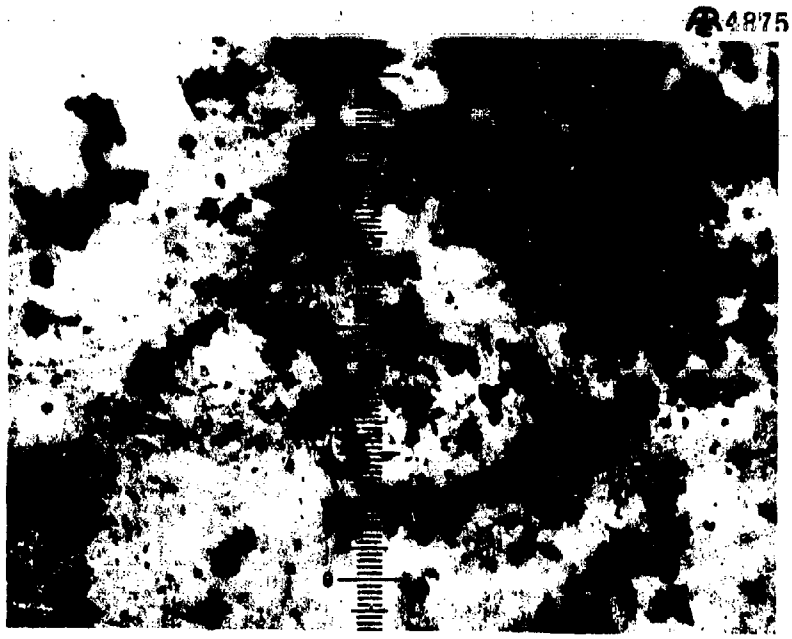
Before Removal of Slurry Bead



After Removal of Slurry Bead

Figure 12. Photomicrographs of Wet Slurry Particle Forcibly Impinged on Dry Paper (Slurry of 73 Per Cent Boron in JP-4), as a Comparison Control Sample.

Each Small Scale Division Equals 4.9 Microns



Before Removal of Large Particles

After Removal of Large Particles

Figure 13. Photomicrographs of Dry Boron Forcibly Impinged on Dry Paper (Boron Ball-Milled 44 Hours), as a Comparison Control Sample.

Each Small Scale Division Equals 4.9 Microns

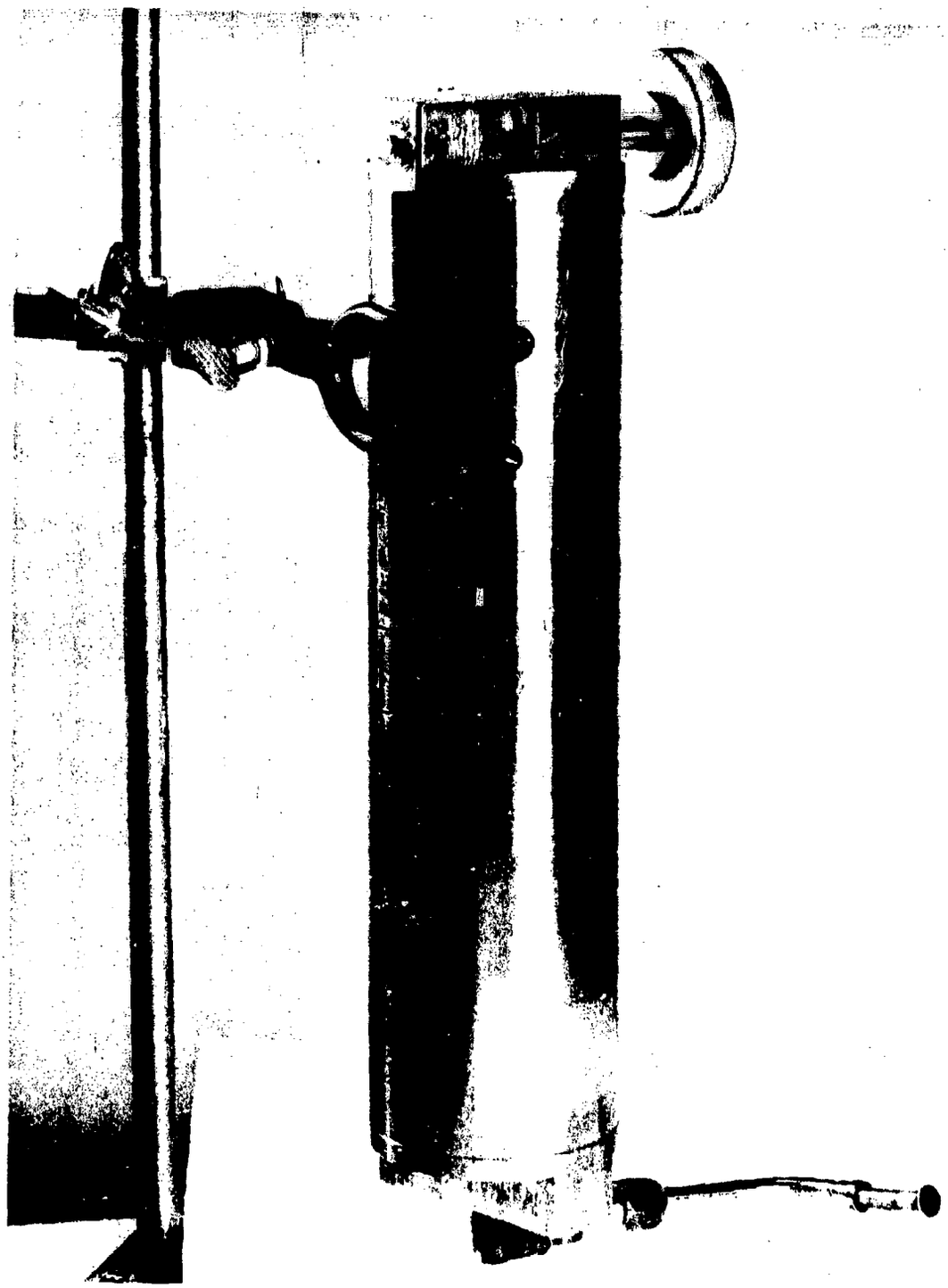


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Figure 14. Assembly Used for Poppet Atomization Tests with Heated and Unheated Boron Slurries (Heater Coil not Shown).

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4865

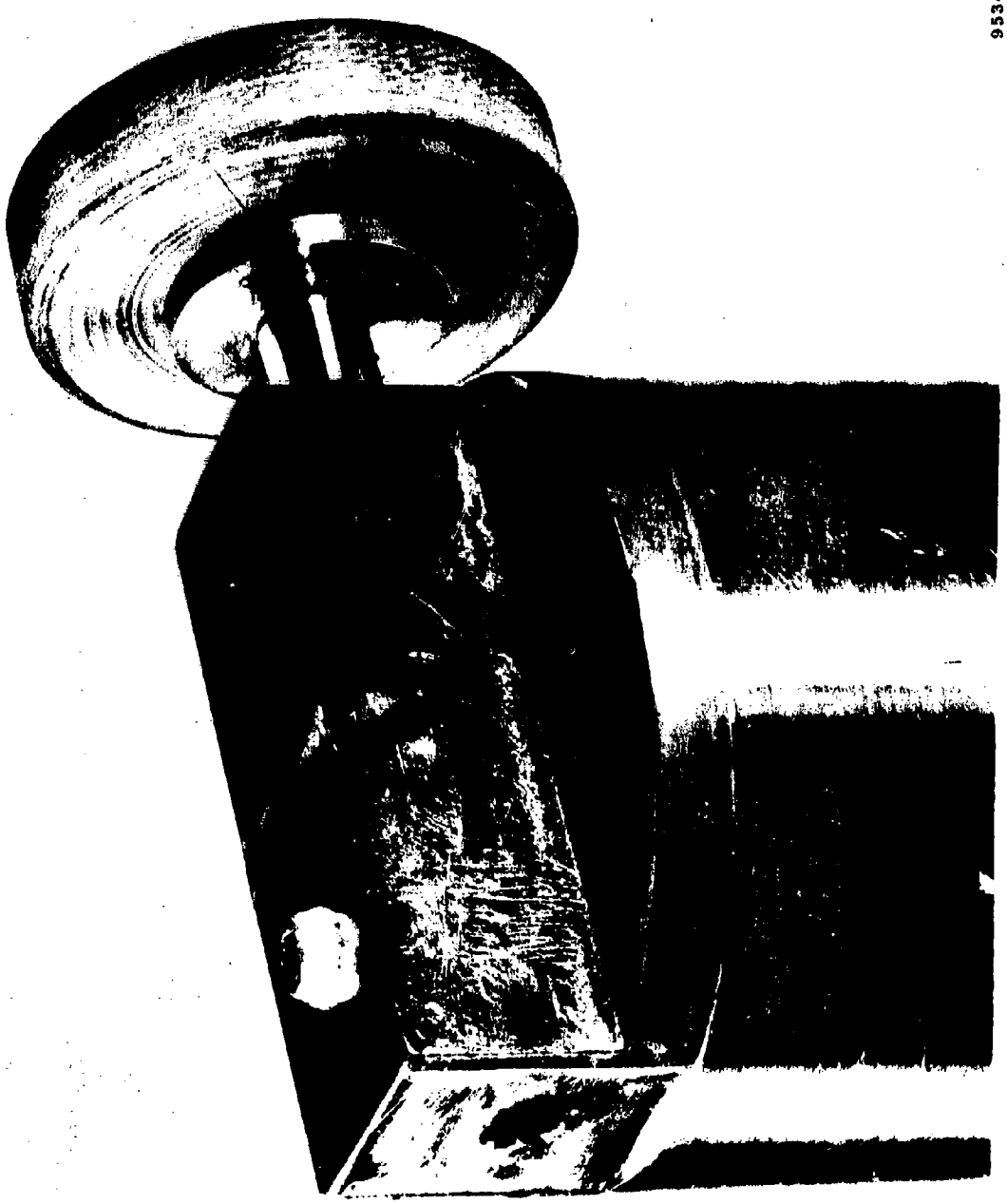

Figure 15. Close-up of Poppet Valve Slurry Atomizer.

The results of the tests are presented on Table XIV. These results indicate that the JP-4-based slurry became hardened under the temperature and pressure conditions used. However, since there was a possibility of carrier leakage, this result is believed to be a false indication of temperature instability (see Section 2.3.1).

The slurry in isopropanol showed no sign of hardening, even though evidence of some carrier loss was present in the form of gummy drainage from the poppet. Expulsion of the isopropanol-based slurry at about 300°F resulted in a very fine cloud of dry dust which would not adhere to dry surfaces. The flow rate was about one pound per second. Photographs of a sample collected on a greased slide near the outlet are presented on Figure 16. The particle sizes are comparable to those obtained from the particle mill with JP-4 based slurry, but were not spherical in shape and were believed to be dry. The non-spheroidicity probably resulted in a higher surface area per unit weight for the poppet-atomized isopropanol slurry than for the particle mill-atomized JP-4 slurry. In the case of the poppet test, there were very few particles over 100 microns in apparent diameter, which would be expected from the violent dispersion associated with the process. Motion pictures of the poppet tests revealed that no significant factors escaped visual observation.

3.3 TESTS WITH ULTRASONICALLY-AUGMENTED NOZZLE

The Hartmann-whistle* nozzle performed very well with water, but was unsuccessful in atomizing thick slurry. When a slurry of 75 per cent boron in isopropanol was forced through the nozzle at about 50 psig (air pressure 100 psig) and a flow rate of about 0.02 pound per second, very large clumps of slurry (~1/8 inch equivalent diameter) resulted. The slurry also agglomerated about the air exit, indicating that the slurry was too thick to be atomized by this method.

Somewhat better success was achieved with a thinner slurry of 73 per cent boron in JP-4. As shown on Figure 17, the slurry particles were

* Trade names and suppliers are contained in Appendix I

TABLE XIV

RESULTS OF POPPET ATOMIZATION TESTS AT SLURRY TEMPERATURE OF 80°F AND 300°F AND 500 PSIG EXPULSION PRESSURE

Test No.	Slurry	Slurry Temperature, °F	Soak Time	Results
1	73% Boron in JP-4	80°F	-	Cone-Shaped Spray of Large Wet Particles
2	73% Boron in JP-4	390°F	Overnight	Slurry Had Formed a Hard Cake, No Discharge
3	75% Boron in Isopropanol	80°F	-	Tubular Extrusion of Slurry, No Breakup
4	75% Boron in Isopropanol	285°F	Overnight	Fine Dust of Apparently Dry Particles
5	75% Boron in Isopropanol	300°F	4 Hours	Fine Dust of Apparently Dry Particles
6	73% Boron in JP-4	310°F	4 Hours	Slurry Had Formed a Hard Cake, No Discharge

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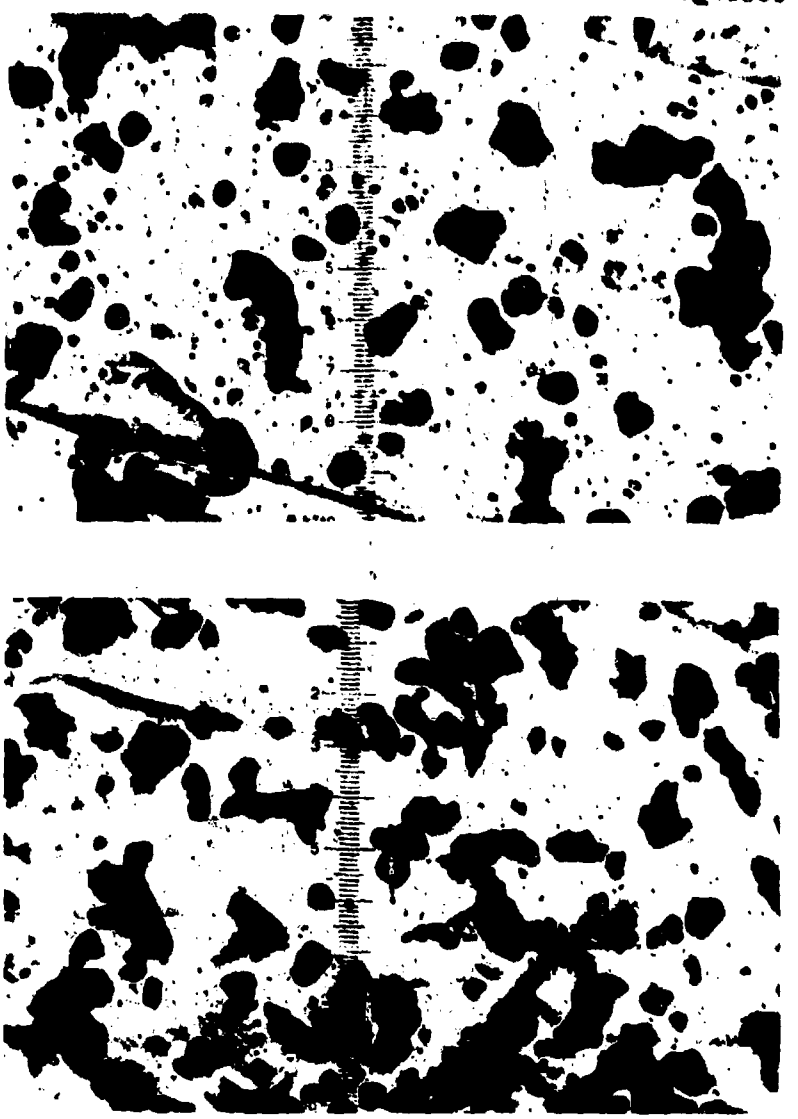
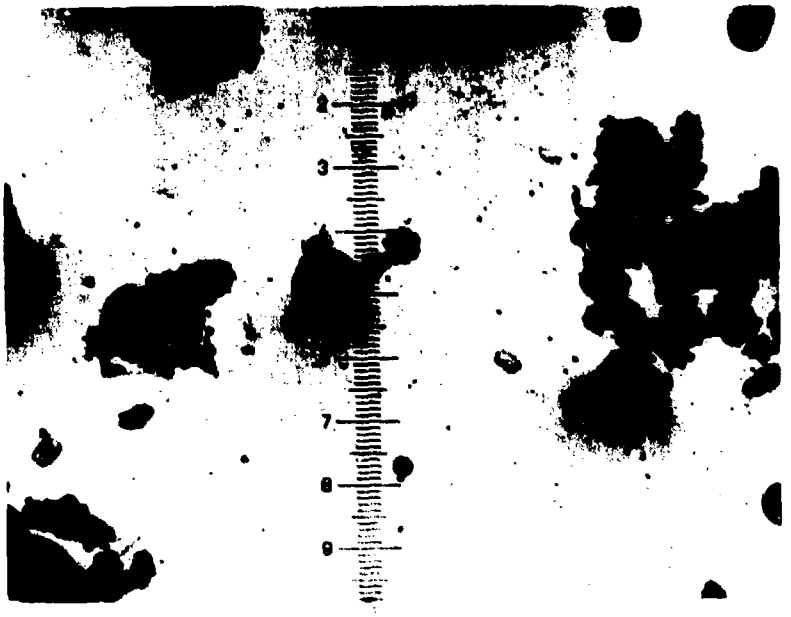


Figure 16. Photomicrographs of Samples Collected from Poppet Atomization of 75 Per Cent Boron-Isopropanol Slurry Heated to 300°F (Ram Pressure was 500 psia).

Each Small Scale Division Equals 4.9 Microns



Each Small Scale Division Equals 17.5 Microns

AR4870

Figure 17. Photomicrograph of Sample of 73 Per Cent Boron-JP-4 Slurry Atomized in an Ultrasonically Augmented Nozzle (Slurry Flow Rate Approximately 0.02 lb/sec), Collected on a Greased Slide.

very large compared with those obtained from the poppet and the particle mill. However, the energy input to the whistle was relatively low and could possibly be increased by a factor of two or three. This type of injection may therefore hold some promise for lightly loaded hydrocarbon-based slurries.

The behavior of the ultrasonically-augmented nozzle was surprisingly similar to that hypothesized for the particle mill. The fuel is injected at low pressure drop, and efficient atomization appears to require either a very low viscosity (and solids loading) or dilation of the slurry during atomization.

3.4 DUAL-FLUID INJECTOR TESTS

The dual-fluid injector used for these tests was the injector that has been used to atomize slurries in the ambient pressure combustor during this program and on Contract No. AF 33(657)-12290. A schematic representation of this injector is presented as Figure 18. The slurry is forced through a tube 0.06 inch in diameter. At the tube exit, air at room temperature is impinged at a right angle onto the slurry stream. The air impinges in the form of a thin, circular sheet. Photomicrographs of samples collected from the isopropanol-based slurry (75 per cent solids) atomized in the dual-fluid injector, at slurry flow rates of 4×10^{-4} and 12×10^{-4} lb/sec, are presented on Figure 19. At these flow rates, the ratios of air to slurry were about 1/2 and 1/6, respectively. The photomicrographs indicate that the dual-fluid atomizer compares very well with the poppet atomizer when the latter is used with heated slurry. There appears to be a larger number of very small particles from the dual-fluid injector than from the poppet. Very little difference can be observed between the samples for the two flow rates. Since the particles from the dual-fluid injector did not adhere to dry surfaces they are assumed to have been dry.

The final tests in this series were performed with JP-4-based slurries atomized in the dual-fluid injector normally used in the ambient

SLURRY ATOMIZER

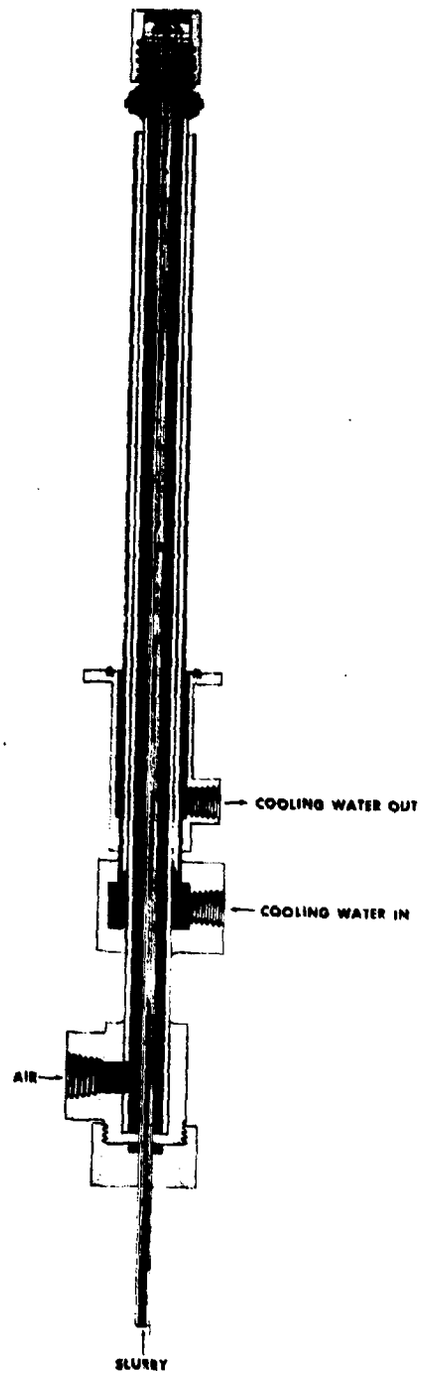


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Figure 18. Cross Section of Slurry Atomizer and Injection Assembly for ARC Slurry Combustor.

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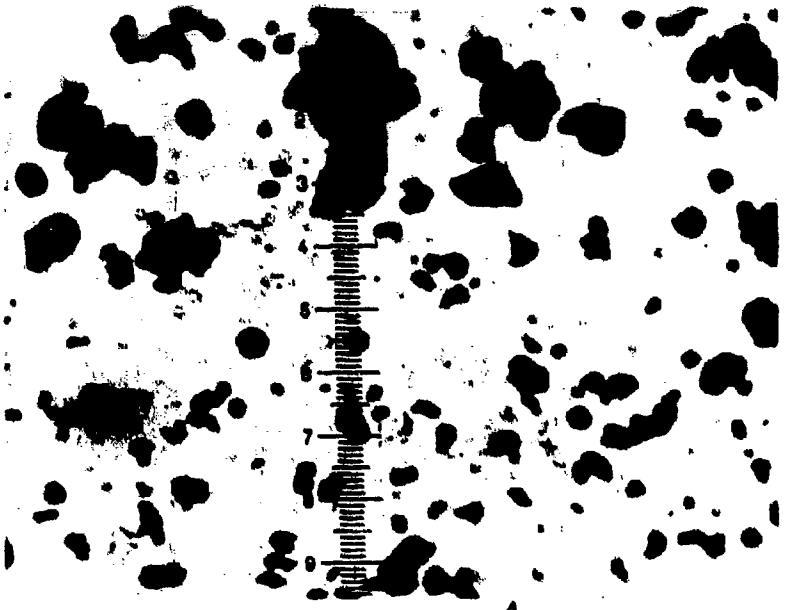
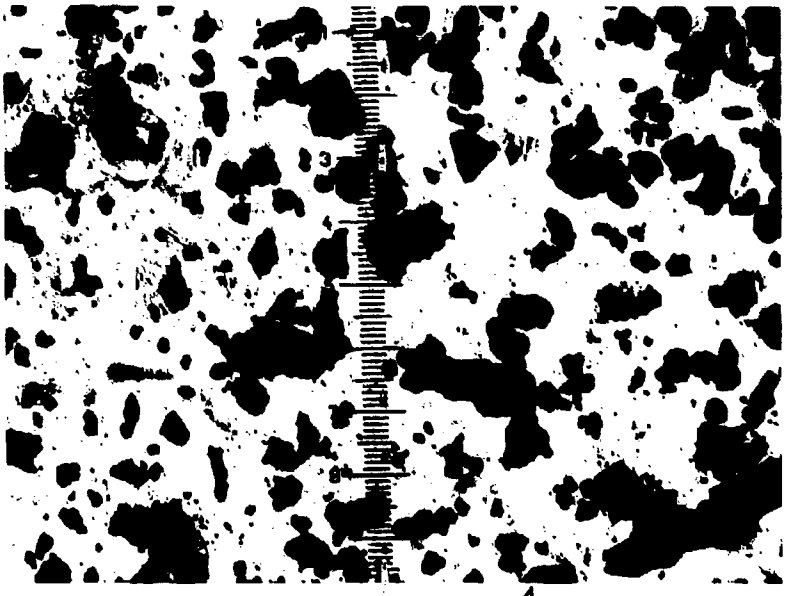


Slurry Flow Rate 4×10^{-4} lb/sec,
Air Flow Rate 2×10^{-4} lb/sec.



Slurry Flow Rate 12×10^{-4} lb/sec,
Air Flow Rate 2×10^{-4} lb/sec.

Figure 19. Photomicrographs of Samples Collected on a Greased Slide from 75 Per Cent Boron-Isopropanol Slurry Atomized in Dual-Fluid Atomizer (Air Temperature 70°F, Each Small Scale Division Equals 4.9 Microns.

pressure combustor. Photomicrographs of particles collected in these tests are presented on Figures 20 and 21 for slurries containing 73 per cent ball-milled commercial boron and 70 per cent ball-milled Callery high-purity boron, respectively. The particle shapes and sizes shown on Figures 20 and 21 compare closely with the sizes and shapes obtained from a similar test using isopropanol-based slurry containing 75 per cent ball-milled commercial boron shown on Figure 19. The particles obtained from atomization of the slurry containing high-purity boron in JP-4 (Figure 21) appear wetter and slightly larger than those of the commercial boron in JP-4 (Figure 20). It is believed that this difference is related to the higher concentration of wetting agent required in the slurry containing high-purity boron (six per cent of the solids) compared to the usual concentration in the commercial boron slurry (three per cent of the solids).

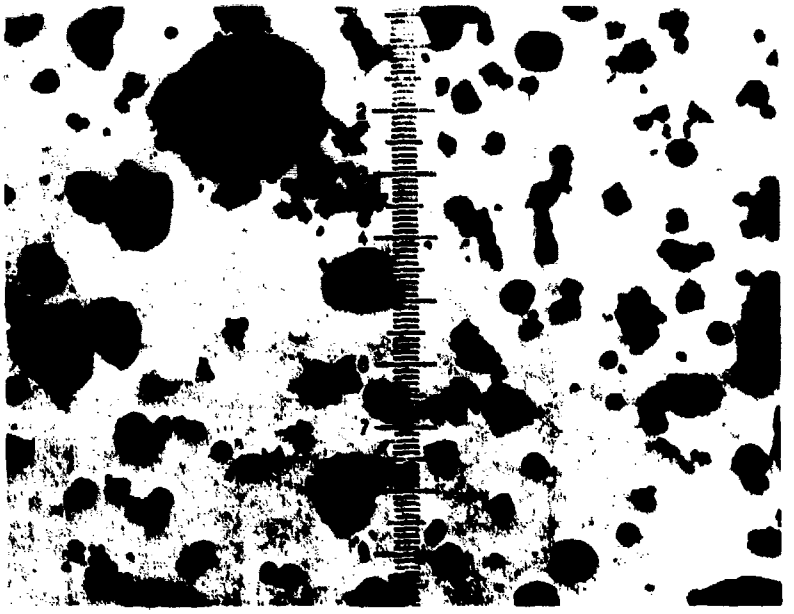
3.5 SELECTION OF SLURRY ATOMIZER FOR EVALUATION TESTS

A summary of the results from the slurry atomization tests is presented on Table XV. Based on this comparison, and on comparison of the photographs of particles collected from the various tests, it was decided that a dual-fluid atomizer similar to the design shown on Figure 18 would offer the least discrimination due to slurry properties. The particles resulting from this atomizer, for both types of slurry used, appeared fairly close in size distribution to the 5 to 50 micron range obtained from the Coulter Counter analyses (Figure 9).

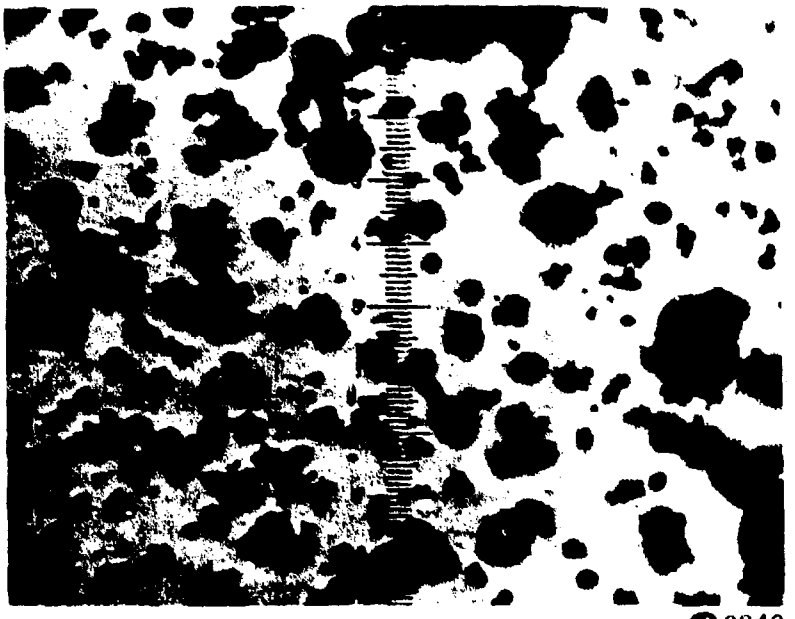
3.6 DISCUSSION OF ATOMIZATION TEST RESULTS

3.6.1 Agglomerate Sizes

Except for the ultrasonic nozzle, the photomicrograph of the atomized slurry from all methods show particle (agglomerate) size ranges from several microns diameter to about 100 microns in diameter, with the major portion of the boron occurring in particles between 25 and 100 microns in diameter or length. The agglomerates resulting from the poppet atomization of the isopropanol-based slurry and from dual-fluid atomization of both isopropanol-based and JP-4-based slurries are much more irregular



Slurry Flow Rate 4 x 10^{-4} lb/sec.
Air Flow Rate 2 x 10^{-4} lb/sec.



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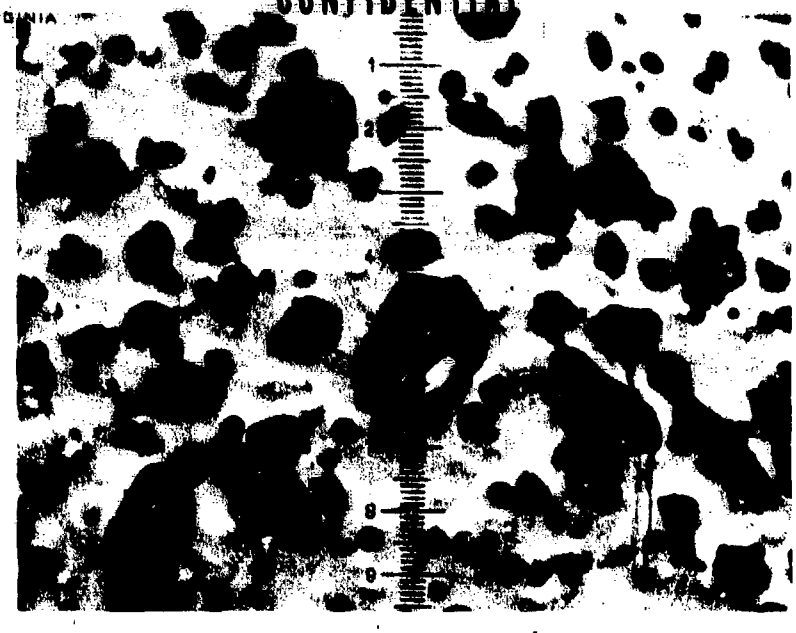
Slurry Flow Rate 12 x 10^{-4} lb/sec.
Air Flow Rate 2 x 10^{-4} lb/sec.

Figure 20. Photomicrographs of Samples Collected on a Greased Slide from 73 Per Cent Boron-JP-4 Slurry Atomized in Dual-Fluid Atomizer. (Air Temperature 70°F, Each Small Scale Division Equals 4.9 Microns).



Slurry Flow Rate 4 x 10^{-4} lb/sec.
Air Flow Rate 2 x 10^{-4} lb/sec.

AR6339

Slurry Flow Rate 12 x 10^{-4} lb/sec.
Air Flow Rate 2 x 10^{-4} lb/sec.

Figure 21. Photomicrographs of Samples Collected on a Greased Slide from 70 Per Cent Boron (Ultra-Fine, High-Purity) in JP-4 Slurry Atomized in Dual-Fluid Atomizer. (Air Temperature 70°F, Each Small Division Equals 4.9 Microns).

TABLE XV

GENERAL RESULTS OF BORON SLURRY ATOMIZATION TESTS

ATOMIZER	SLURRY	CONDITIONS	RESULTS
Particle Mill	73% Boron in JP-4	Air Temp. 600°F; Slurry and Air Flow Rates both 0.2 lb/sec.	Bulk of boron in particles 25 to 150 microns in diameter. Large particles up to 2,000 microns were collected. All larger particles (above 50 μ) appeared wet.
Particle Mill	75% Boron in Isopropanol	Air Temp. 600°F; (Results observed during 1964 Micro-Ramjet Test Series)	Observed many large particles issuing from nozzle prior to ignition in combustion tests.
Ultrasonic	75% Boron in Isopropanol	Slurry Flow Rate about 0.02 lb/sec. Air Pressure up to 200 psig.	Poor slurry breakup; most particles about 1/8-inch in diameter.
Ultrasonic	73% Boron in JP-4	Slurry Flow Rate about 0.02 lb/sec. Air pressure up to 200 psig	Slurry was broken up, but resulting particles were relatively large. Many were 2,000 to 5,000 μ (up to 1/8-inch) in diameter.
Poppet	73% Boron in JP-4	Soaked at 300°F, 500 psig for four hours or longer	Slurry would not flow (two tests).
Poppet	75% Boron in Isopropanol	Soaked at 300°F, 500 psig for four hours or longer. Flow rate about 1 lb/sec	Opening the poppet valve released a cloud of fine, dry atomized slurry. The largest particles were about 100 μ in diameter. Most of the particles remained suspended in the air.
Poppet	73% Boron in JP-4 75% Boron in Isopropanol	Ambient temperature, 500 psig	Isopropanol-based slurry was extruded as a continuous tube; JP-4-based slurry produced large particles (up to 1/4-inch in diameter).

TABLE XV
(continued)

ATOMIZER	SLURRY	CONDITIONS	RESULTS
Dual-Fluid	75% Boron in Isopropanol	Conditions Given On Figure 19.	Particle sizes comparable to poppet results for the same slurry. Most of the boron present as 25-100μ particles. The particles were not spherical and appeared dry.
Dual-Fluid	73% Boron in JP-4 70% Callery Boron in JP-4	Conditions Given on Figures 20 and 21	Particle sizes and shapes similar to those for the isopropanol-based slurry in this atomizer.

in shape than those resulting from particle mill atomization of the JP-4-based slurry. This would result in a greater exposure of surface available for burning for particles atomized by the poppet and dual-fluid atomization methods. In addition, a significant number of very large particles, up to several thousand microns in diameter, were collected in the particle mill tests with JP-4 based slurry. The poppet and the dual-fluid atomizers therefore provided the most efficient atomization for the test sizes and conditions used. Atomization efficiencies of the dual-fluid atomizer will, of course, depend on the ratio of air to slurry, and may also be affected by the size of the slurry stream to be broken up.

3.6.2 Nature of Agglomerates

The agglomerates produced from atomization are, on the average, larger than the agglomerates present in the slurry. Whereas, the agglomerates in wet slurry (primary agglomerates) result from ball-milling and consist of primary boron particles held together by an adhesive of oxidized boron; the agglomerates resulting from atomization consist of primary agglomerates (those originally in the slurry) held together by wetting agent, carrier residues, and other materials remaining after the carrier is vaporized. It appears that the agglomerate sizes resulting from atomization should be a function of slurry formulation, but for the two slurries tested this has not been the general case. It is likely that such a dependence, if one exists, would become important only as the result of atomization that is much more efficient than that afforded by the techniques considered in this program.

3.6.3 Breakup of Primary Agglomerates

In several of the photomicrographs of atomized slurry (for instance, Figure 19), it was noted that many extremely fine particles on the order of one micron in diameter were present. Since this size range is more representative of primary boron particles (0.7 - 1.5μ from the Coulter Counter analysis), it seemed likely that some of the primary agglomerates had been broken up by the shearing action of the various atomizers.

In order to determine the extent of agglomerate breakup during atomization, samples of atomized slurry collected during the tests with the poppet atomizer (isopropanol-based slurry) and the particle mill (JP-4-based slurry were analyzed with the Coulter Counter. The collected particles were dispersed in butanol-benzene mixture which was expected to dissolve the wetting agent and similar materials but would not dissolve oxides of boron to any appreciable extent.

Comparison of the primary agglomerate size distributions before and after atomization of the slurries are presented on Figures 22 and 23 for slurries of 73 per cent ball-milled commercial boron in JP-4 and 75 per cent ball-milled commercial boron in isopropanol, respectively. Significantprimary agglomerate breakup during atomization is evident for both slurries, and the breakup is more pronounced for the poppet-atomized slurry in isopropanol. It is also obvious from Figure 22 that not all of the binding material from the JP-4-based slurry was dissolved in the butanol-benzene mixture, resulting in larger particle sizes than those present in the slurry prior to atomization. These results lend credibility to the possibility of reducing the particle sizes entering the combustion chamber (as a result of atomization of slurries containing ball-milled boron) through very efficient, high shear atomization techniques.

3.7 TESTS WITH DUAL-FLUID INJECTOR

Several cold flow tests were performed with the dual-fluid injector designed for the micro-ramjet engine, in order to study the atomization and to compare particle sizes obtained from the new injector with previous results obtained from particle mill atomization. The results of microscopic examination of samples of atomized slurry (73 per cent ball-milled boron in JP-4) resulting from the dual-fluid cold flow tests are shown on Table XVI. Photographs of the samples collected from the dual-fluid atomizer are shown on Figure 24. In these tests the ratio of atomizer air to slurry was varied from 1.8 to 0.7, which is comparable to the previous test with the particle mill in which the ratio of air to slurry was 1.0. The most important difference between the conditions of

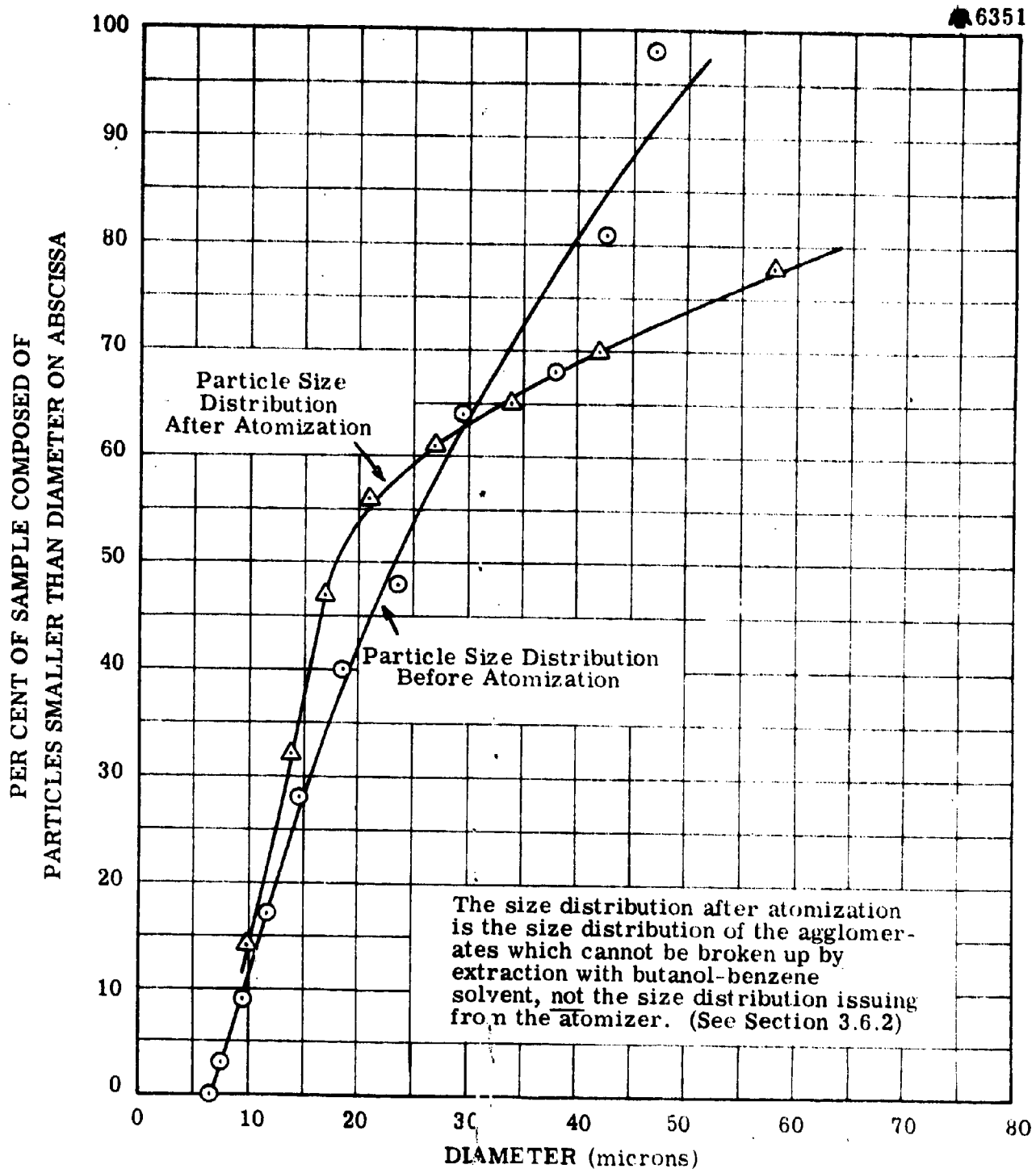


Figure 22. Comparison of Primary Agglomerate Size Distribution Present in Slurry of 73 Per Cent Ball-Milled Boron in JP-4 Before and After Atomization by a 4-inch Particle Mill.

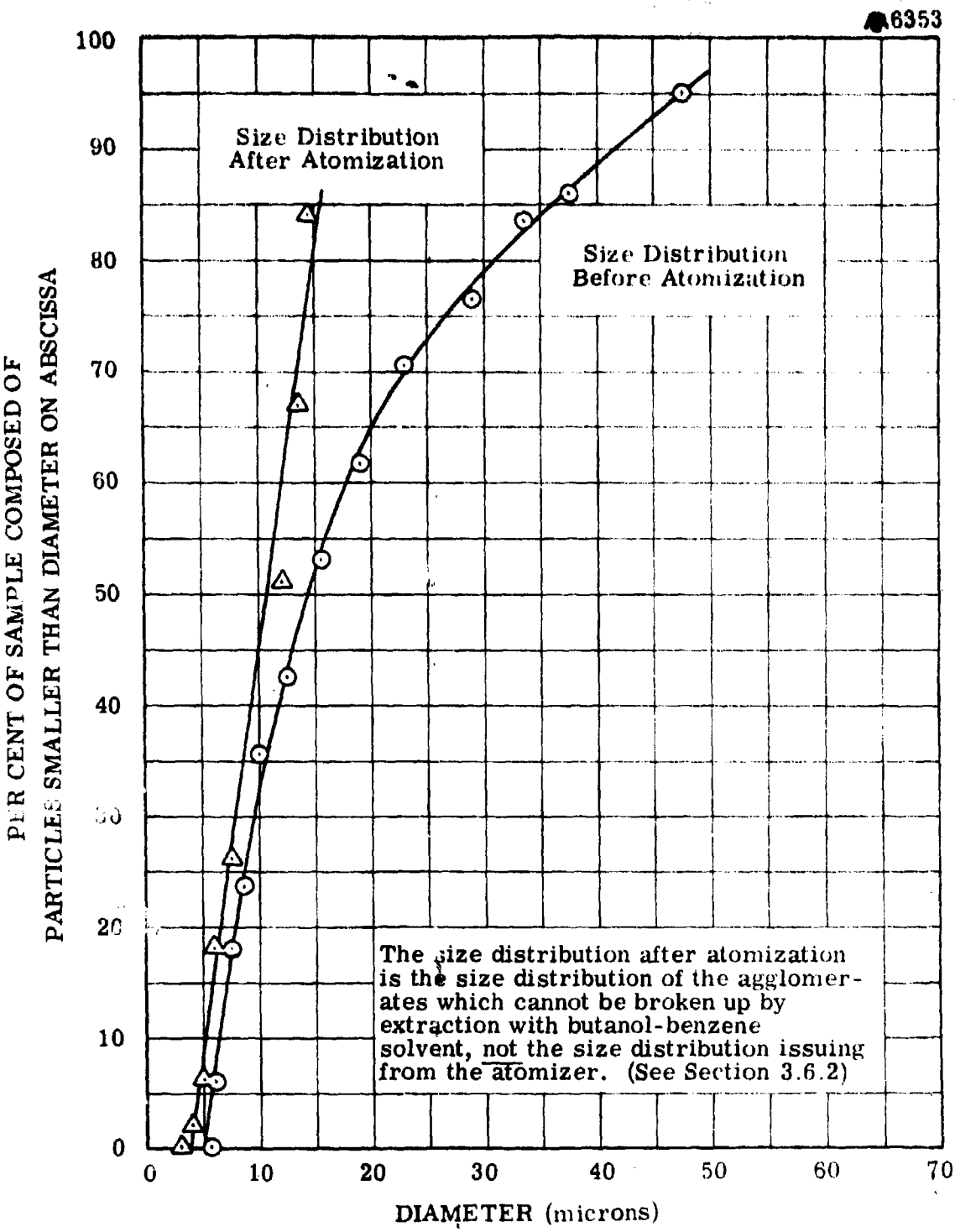


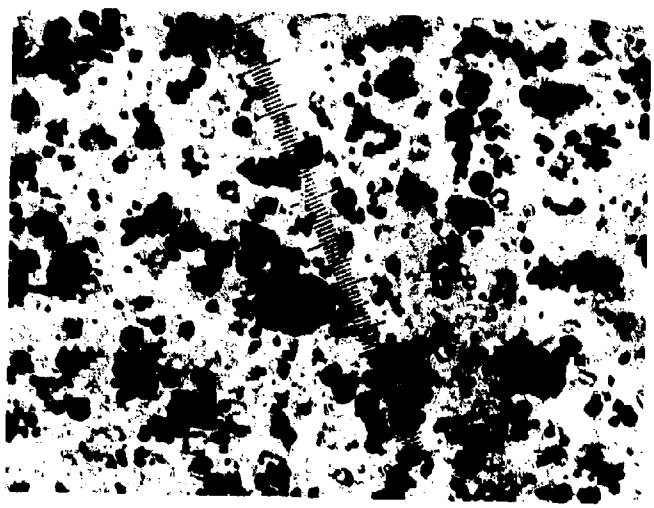
Figure 23. Comparison of Primary Agglomerate Size Distribution Present in Slurry of 75 Per Cent Ball-Milled Boron in Isopropanol Before and After Atomization by a Poppet Atomizer.

TABLE XVI

SUMMARY OF COLD FLOW ATOMIZATION TESTS WITH THE DUAL-FLUID ATOMIZER TO BE USED ON THE MICRO-RAMJET TEST ENGINE (APPROXIMATE AIR TEMPERATURE 100°F; SLURRY TEMPERATURE 80°F; SLURRY OF 73 PER CENT BALL-MILLED BORON IN JP-4

Air Pressure psig	Approximate Air Flow Rate lb/sec	Slurry Flow Rate lb/sec.	Results of Microscopic Examination
500	0.10	0.056	Most particles 5 to 20μ; Largest particles about 50 μ in diameter
400	0.08	0.056	Most particles 10 to 20μ; Some large particles up to 70 μ in diameter
300	0.06	0.056	Most particles 10 to 50 μ; Some large particles up to 100μ in diameter
200	0.04	0.056	Most particles 10 to 50 μ; Some large particles up to 100μ in diameter.

Air Flow Rate 0.04 lb/sec
Slurry Flow Rate 0.056 lb/sec



Air Flow Rate 0.10 lb/sec
Slurry Flow Rate 0.056 lb/sec

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Figure 24. Photomicrographs of Atomized Boron Slurry (73 Per Cent Solids in JP-4) Collected, After Breakup by Dual-Fluid Atomizer, on Greased Slides. Each Small Division Equals 4.9 Microns.

the dual-fluid atomization test and the particle mill test was the air temperature, which was slightly higher than ambient ($\sim 100^{\circ}F$) for the dual-fluid test and $600^{\circ}F$ for the particle mill test. It should be noted here that collection of particles by impingement on a greased slide, which was the method used to obtain particulate samples from the cold flow atomization tests, will result in an accurate count of the larger particles only. In this type of sampling method, and especially in the case of relatively low stream velocities, many of the smaller particles will follow the flow stream lines and will escape around the sampling body.

The results on Table XVI indicate that dual-fluid atomization resulted in a major particle size range of 10 to 50 microns, which was approximately one-half the size of those resulting from particle mill atomization (bulk of the boron in particles 25 to 100 microns in diameter). All of the particles resulting from dual-fluid atomization were strikingly spherical, in contrast to the roughly-shaped particles resulting from all of the laboratory injection tests. A trend towards larger particles with decreasing air flow rate is evident from the observations presented on Table XVI. This trend substantiates the hypothesis that successful atomization of boron slurries will require the maximum amount of energy, including heat energy, being made available to the slurry before and during the atomization process.

The results of these cold flow tests indicate that, under similar conditions of fuel-to-air-ratio, the present dual-fluid injector is more efficient in atomizing JP-4-based boron slurry than the particle mill used on the micro-ramjet engine in other combustion tests under this program. The use of hot gas instead of cold air (or any other method of adding energy to the system) would be expected to make the dual-fluid atomization even more efficient, especially in terms of the amount of secondary fluid required to achieve a desired particle size for a given slurry flow rate.

4.0 COMBUSTION TESTING AND SLURRY EVALUATION

The following three general types of combustion testing of boron slurries were performed during the program:

(1) Ambient pressure combustion testing in which the relative chemical reactivity of atomized slurry (dual-fluid atomization) was determined;

(2) Base line combustion tests and slurry evaluation tests in the 3.5-inch micro-ramjet equipped with particle mill injection;

(3) Checkout tests and slurry evaluation tests in the 3.5-inch micro-ramjet equipped with dual fluid injection.

The objectives of the combustion testing program were as follows:

(1) To establish a correlation between the results of ambient pressure combustion tests and ramjet combustion tests under simulated flight conditions;

(2) To establish a base line for comparison of combustion data from the micro-ramjet with test data obtained at the Marquardt facility;

(3) To develop and utilize methods of evaluating slurry combustion performance which would not discriminate between slurries on the basis of physical or rheological characteristics of the slurries;

(4) To evaluate the combustion performance or potential of formulations using several types of atomization methods, in order to study various possible methods of enhancing slurry combustibility.

A secondary objective of the combustion studies was to obtain insight into the processes which occur when boron is combusted with air, based on observations of the combustion tests and exploratory experiments with the micro-ramjet test engine.

4.1 AMBIENT PRESSURE COMBUSTION TESTS

4.1.1 Background and Previous Work

The ambient pressure combustion tests consisted of determining plots of combustion efficiency of boron versus air preheat temperature for boron slurry samples which had been injected into a heated air stream through a dual-fluid atomizer. The fuel-air mixture was kept extremely lean (fuel-to-air ratio about 0.006) to minimize effects of oxygen depletion and temperature increases due to the combustion of the atomized slurry. The combustion efficiency of the boron was determined by chemical analysis of exhaust samples collected isokinetically at the outlet of the reaction tube.

A detailed description of the apparatus and experimental procedure, including the chemical analysis of the exhaust samples, is presented in Reference 2. The dual-fluid atomizer used in these tests is also pictured in Figure 18 of this report.

The following conditions apply for all of the ambient pressure combustion tests performed under this program:

Fuel-to-Air Ratio	0.006 lb/lb (Approximate)
Air Flow Rate	0.03 lb/sec
Burner Volume	31.4 cu. in.
Residence Time	6 to 12 millisec.
Air Preheat Temperature	2,000°R to 4,000°R (in steps of 200°R)

Comparison of the plots of chemical combustion efficiency of the boron versus air preheat temperature provided a relative ranking of the combustibility of the atomized slurries. Ambient pressure combustion testing of various slurries under Contract No. AF 33(657)-12290[2], revealed that large differences in combustibility occur among slurry formulations. Combustibility appeared to be enhanced by the use of small particle sizes in the slurry and by boron pre-treatment consisting of

removal of part of all or the oxidized boron and water present at the surface of the boron.

In this program the ambient pressure combustor tests were used for the following two purposes:

(1) To screen experimental slurry formulations for possible adverse or beneficial effects of formulation variables on slurry combustibility (with emphasis on the effect of ultra-fine boron on slurry combustibility); and

(2) To aid in establishing a correlation between the results of the ambient pressure combustion tests and the combustion tests in the micro-ramjet engine.

The screening experiments are described in the following paragraphs. The correlation work is discussed in later sections of the report.

4.1.2 Tests with Ultra-Fine Boron Slurries

Ambient pressure combustion tests were performed with several slurries containing ultra-fine boron powders. Formulation data for these slurries are presented on Table XVII. Both particle size ranges of ultra-fine boron, 50Å to 150Å (high purity, ultra-fine boron), and 500Å (submicron boron), were used in slurries of 50 per cent solids in isopropanol. The results of these tests, which are compared with results with commercial boron slurries at the 50 per cent solids level on Figure 25, indicate that the use of ultra-fine boron resulted in higher combustion efficiencies at the lower preheat temperatures than those observed for commercial boron. However, the combustion efficiencies for the ultra-fine boron were lower than those for commercial boron at the higher preheat temperatures. The unusual shapes of the plots suggested that analytical errors may have been present for the two slurries of ultra-fine boron in isopropanol. These errors, which are believed to have been caused both by procedural errors and reagent degradation, were corrected before the

TABLE XVII

FORMULATIONS[1] USED IN AMBIENT PRESSURE COMBUSTION TESTING OF SLURRIES LIGHTLY LOADED WITH HIGH PURITY BORON

Slurry No.	Type of boron	Formulation
1	Commercial Grade (Wet ball-milled, vacuum dried)	50% Boron (90-92% pure) 50% Isopropanol
2	Ultra-Fine, High Purity (Bulk density increased by shaking 24 hours)	50.45% Boron 52.30% Isopropanol 4.18% JP-4 3.07% Wetting Agent
3	Submicron (Bulk density increased by shaking 24 hours)	50% Boron 48.5% Isopropanol 1.5% Wetting Agent
4	Submicron (Bulk density increased by shaking 4 hours)	50% Boron 47.5% JP-4 1.5% Wetting Agent 1.0% Gellant
5	Commercial (As received)	50% Boron (90-92% pure) 50% Isopropanol

1. More complete formulation data can be found in Reference 1.

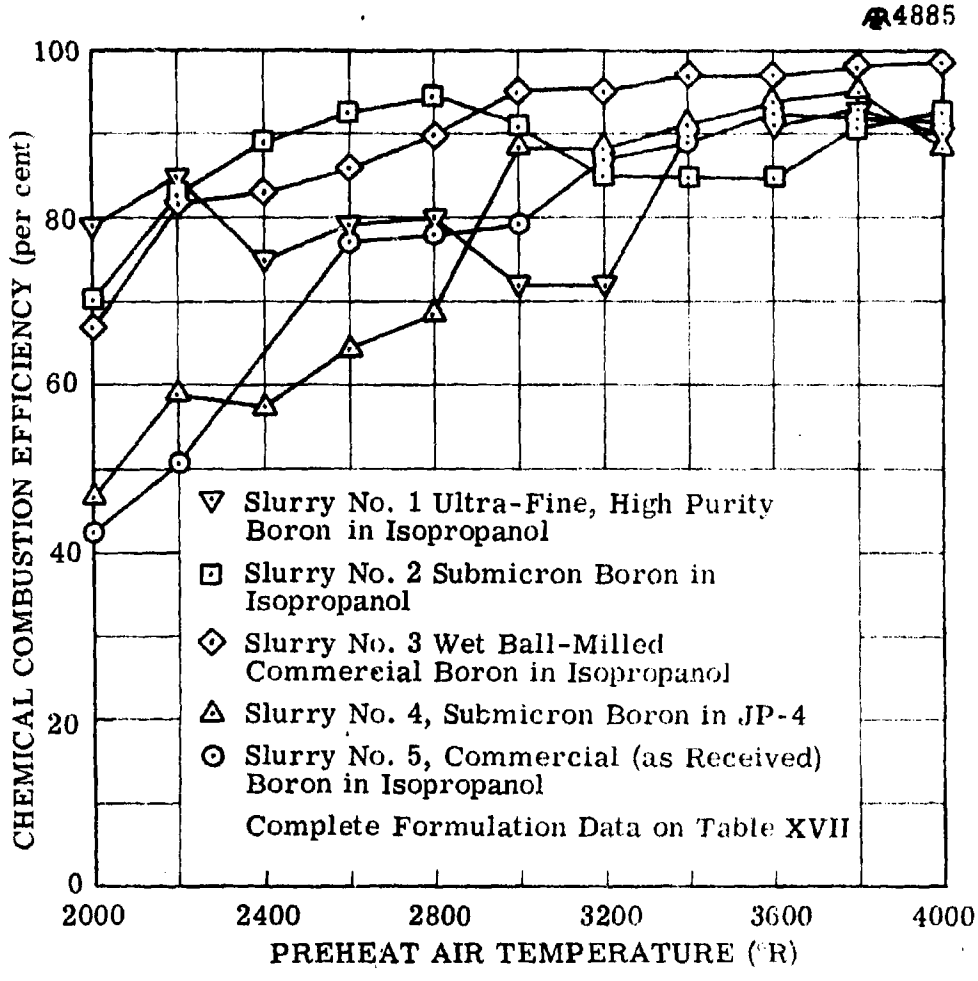

Figure 25. Comparison of Ambient Pressure Combustion Data for Five Boron Slurries at 50 Per Cent Solids Loading.

two least-active slurries were tested. The slurry of wet ball-milled commercial boron was tested in 1964 under Contract No. AF 33(657)-12290[2].

The questionable results on Figure 25 for the slurry containing ultra-fine, high-purity boron were checked by a duplicate run. The results, which are compared with results for a similar loading of as-received (unwashed) commercial boron in isopropanol, are presented on Figure 26. These data indicate that the chemical combustion efficiencies shown on Figure 25 for high purity boron slurries at the lower preheat temperatures may have been erroneously high. However, the high purity boron slurries still showed somewhat higher activities at the lower preheat temperatures than the slurry compounded with as-received commercial boron. Essentially no difference was detected between slurries containing shaken and ball-milled high purity boron.

On Figure 26, the slurry containing 61.1 per cent ultra-fine, high purity boron in JP-4 was equivalent to the isopropanol slurries having lower loadings at lower preheat temperatures, but showed lower combustion efficiencies at the higher temperatures. Presently, no explanation can be given for these results. Since the results at the lower temperatures are probably more significant than those for the higher temperatures, the results may indicate a small effect of solids loading on activity for slurries containing high purity boron.

A comparison of ambient pressure combustion results obtained for a slurry of 70 per cent high purity, ultra-fine boron (ball-milled 97 hours) in JP-4 with results from a slurry of 73 per cent commercial boron (ball-milled 44 hours) in JP-4 is presented on Figure 27. These results show that the slurry containing the high purity boron was slightly less active than the slurry containing the commercial boron. The lower activity of the slurry containing high purity boron is attributed to the high concentration of wetting agent present, which probably caused this slurry to be atomized less efficiently than the slurry containing commercial boron and less wetting agent.

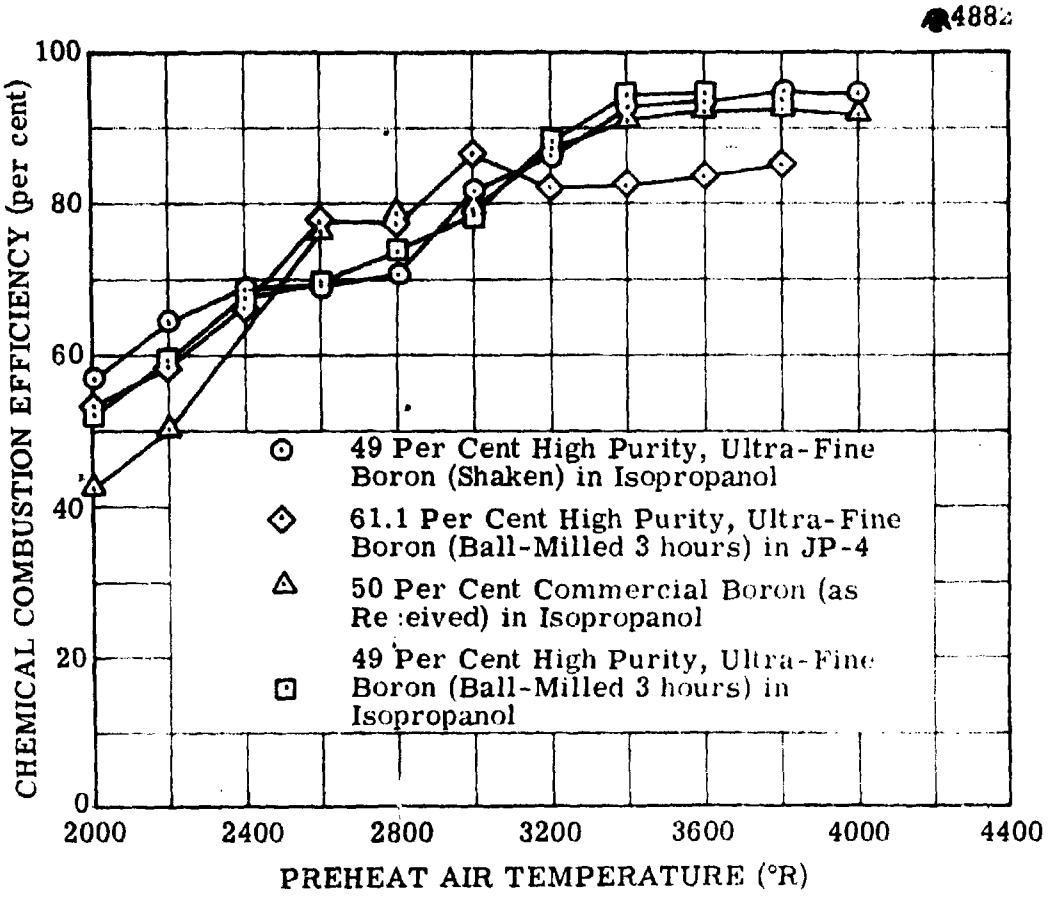

Figure 26. Comparison of Ambient Pressure Combustor Results for Lightly Loaded Slurries Containing Either Ultra-Fine High Purity or As-Received Commercial Grade Boron.

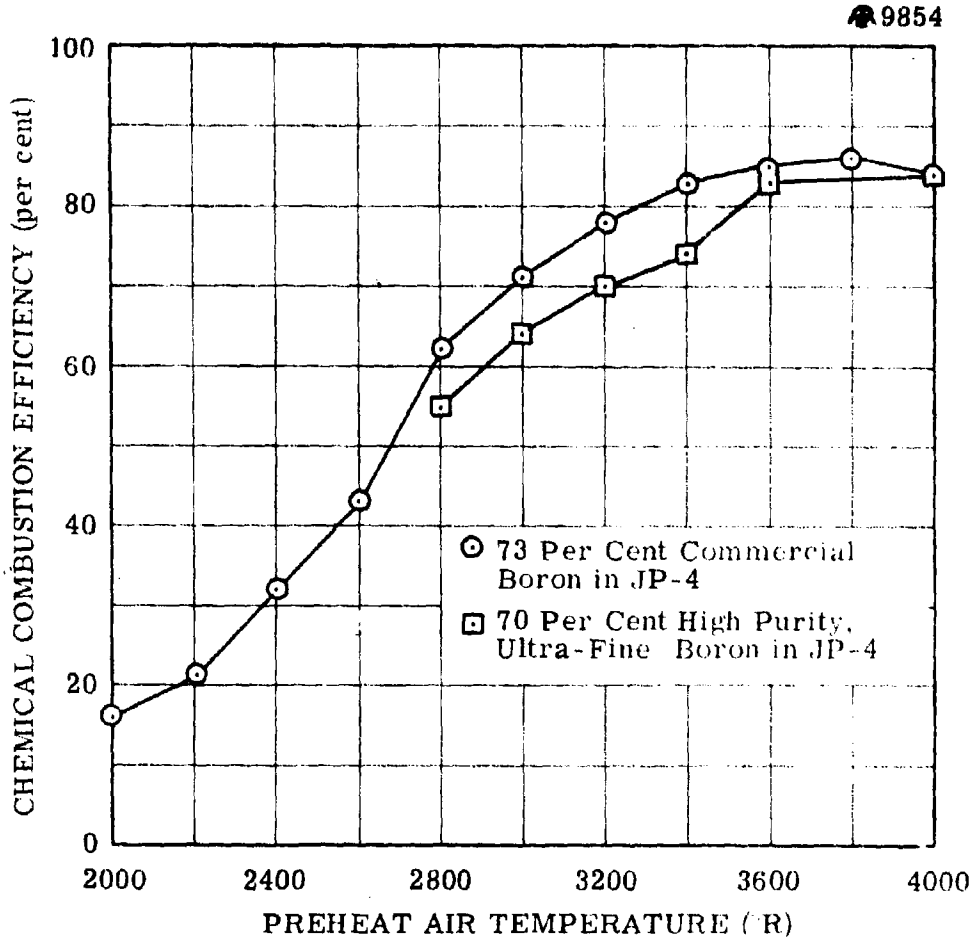

Figure 27. Comparison of Ambient Pressure Combustor Results for Slurries of Commercial Boron and High Purity, Ultra-Fine Boron in JP-4 Carrier.

4.1.3 Testing of 1965 "Workhorse" Formulation

The ambient pressure combustor data for the 73 per cent boron JP-4 slurry (1964 "workhorse" formulation), from Figure 27, are compared with data for the optimized 1965 "workhorse" formulation on Figure 28. The two plots are similar at the lower preheat temperatures, but diverge at the higher preheat temperatures, with the optimized formulation showing less complete combustion than the standard formulation at the higher temperatures. The difference between the plots on Figure 28 is attributed to the higher concentration of gellant present in the optimized formulation. The gellant concentration was increased in order to stabilize the formulation during storage. It should be noted that a reduction of chemical activity due to gellant type and/or concentration has not been observed in previous studies with the ambient pressure combustor. The formulations of the two slurries described on Figure 28 are presented in Table XVIII.

4.1.4 Effect of Lithium Metal Additive

Figure 29 shows the effect of adding lithium metal powder on the combustion efficiency of a slurry of ball-milled boron in JP-4. Enhancement of slurry activity was noted throughout the range of preheat temperature, but the most significant, consistent improvement appeared to occur at the higher values of preheat temperature. This was the most active slurry containing dry ball-milled boron yet tested, and, although the lithium concentration was higher (10.5 per cent of the solids) than that which could be practically utilized because of the low density of lithium, lithium powder must be considered the most promising solid additive tested to date.

4.1.5 Testing of Washed Boron Slurries

In previous work[2] on washing (or wet ball-milling) of boron followed by vacuum drying, it was noted that the consistency of the dried material varied from a fluffy powder to a hard, solid cake even when the

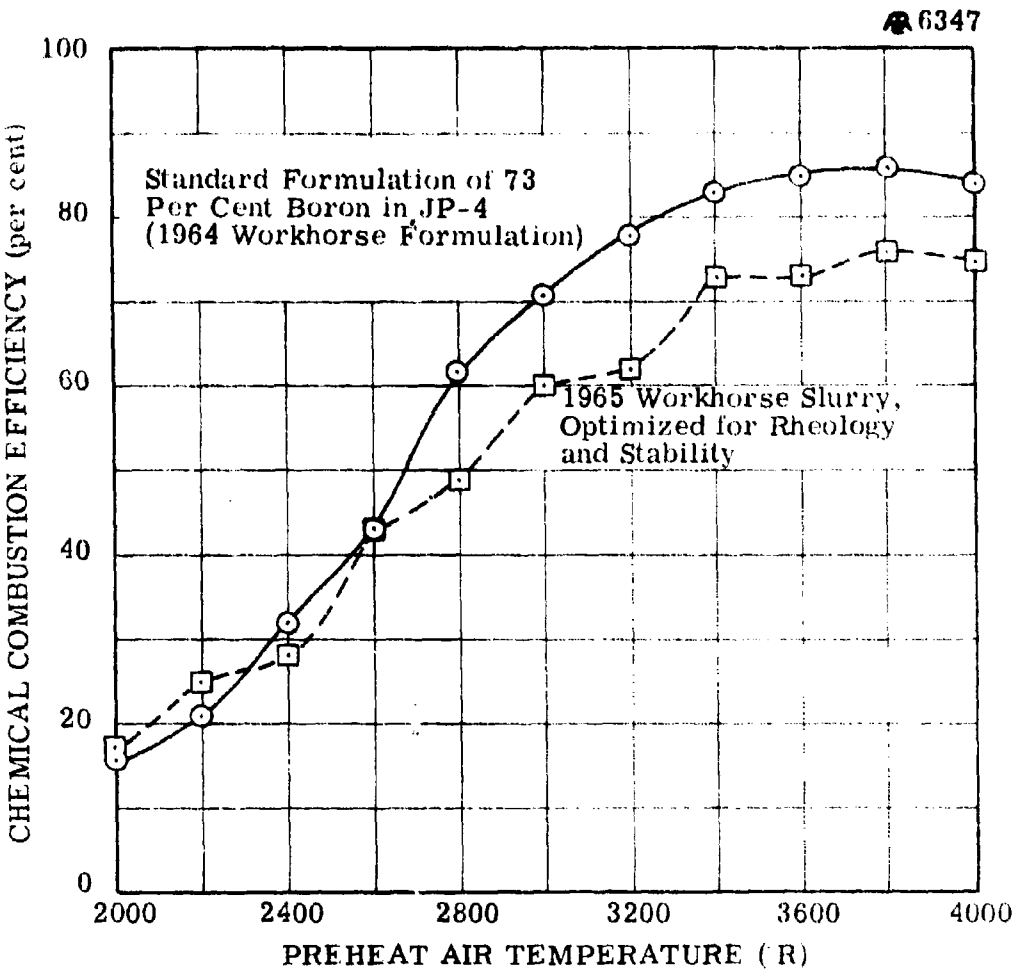

Figure 28. Comparison of Ambient Pressure Data for two Slurries of 73 Per Cent Ball-Milled Boron in JP-4. (Formulation Data are in Table XVIII.

TABLE XVIII

FORMULATION DATA FOR COMPARISON OF WORKHORSE SLURRIES TESTED ON THE AMBIENT PRESSURE COMBUSTOR

STANDARD JP-4-BASED SLURRY

Boron (44-hour ball-milled)	73.0%
Wetting Agent (Glycerol Sorbitan Laurate)	3.0%
Gellant (Aluminum Soap)	0.5%
JP-4 Carrier	23.5%
	100.0%

OPTIMIZED "WORKHORSE" FORMULATION

Boron (44-hour ball-milled)	73.0%
Wetting Agent (Glycerol Sorbitan Laurate)	2.19%
Gellant (Modified Polystyrene)	0.99%
JP-4 Carrier	23.82%
	100.00%

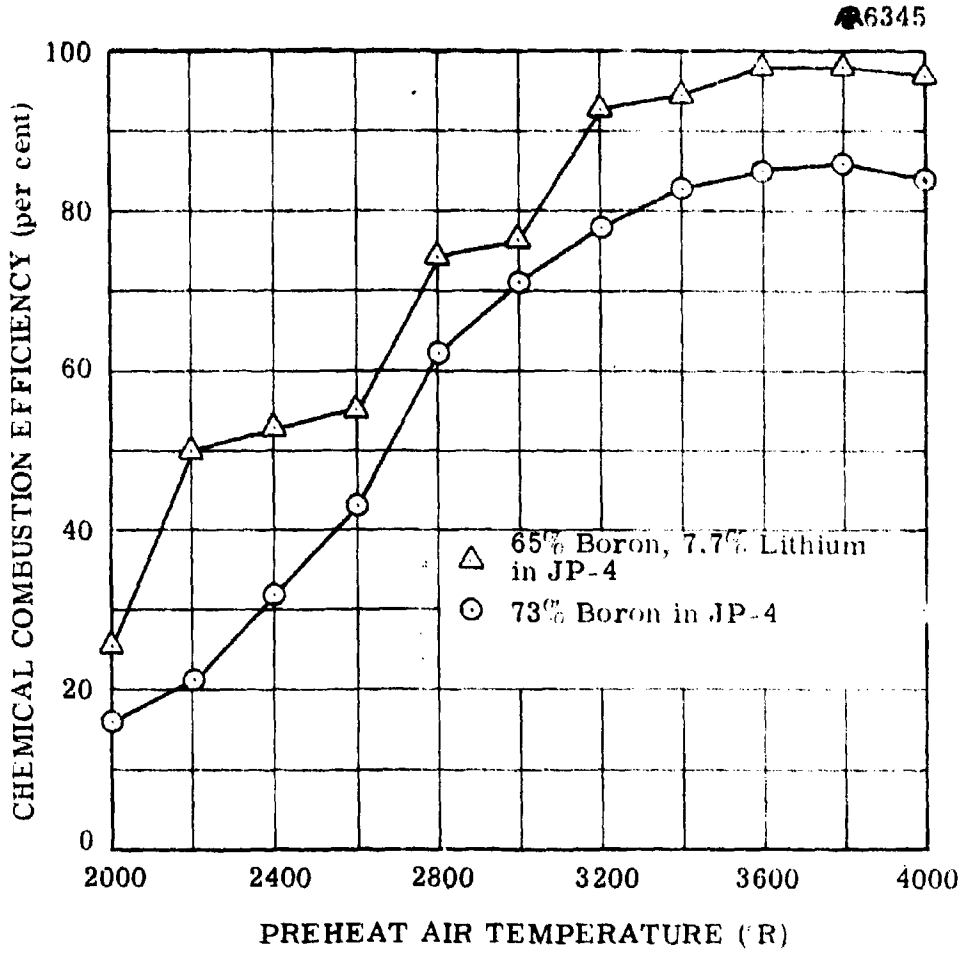

Figure 29. Comparison of Ambient Pressure Combustor Results for Slurries of Commercial Boron, and Commercial Boron with Lithium Additive, in JP-4 Carrier.

washing and drying conditions were the same, within reasonable limits of experimental error. Experimentation along this line was so severely limited by the non-reproducibility that no extensive studies were performed, even though slurries made with washed commercial boron have been among the most active slurries tested in the ambient pressure combustor[2]. Because of the high activity of the slurries made with washed boron, an attempt was made during this program to formulate a washed boron slurry with a particle size distribution (resulting from breaking up a dried cake of washed boron) which would allow solids loadings of 75 per cent or higher.

The present work involved the washing and drying of two batches of boron of about two pounds each. One sample had been dry ball-milled 44 hours, and the other 100 hours. After four washings (three with hot 0.01 N HCl and the fourth with hot water) and drying in a vacuum oven (150°C, full vacuum) for 30 hours, both batches were solid cakes of agglomerated boron particles. The cakes were broken up with a hammer, screened through window screen (holes about 3/32-inch square), and mixed together. A slurry containing 50 per cent of this material in isopropanol was prepared for ambient pressure combustion testing and particle size analysis. The slurry was extremely grainy. A similar slurry in JP-4 carrier was even more grainy, probably because of less dissolution of the binding material by JP-4 than by alcohol.

The results of the combustion test on the isopropanol-based slurry sample are compared with those for a similar slurry made with unwashed (as-received) commercial boron on Figure 30. The poor combustion was undoubtedly due to the presence of large agglomerates of boron which were visible in the exhaust samples. Particles as large as 1/16-inch in diameter were observed in the samples. The particle-size analysis by the Coulter Counter method using a nonaqueous carrier (benzene-butanol mixture made conductive with NH_4CNS) is shown on Figure 31. The most frequent size registered was about 10 microns, with other sizes ranging up to 30 microns. It was subsequently found that the slurry sample used in the Coulter analysis was the top of a large volume of slurry which had been stored

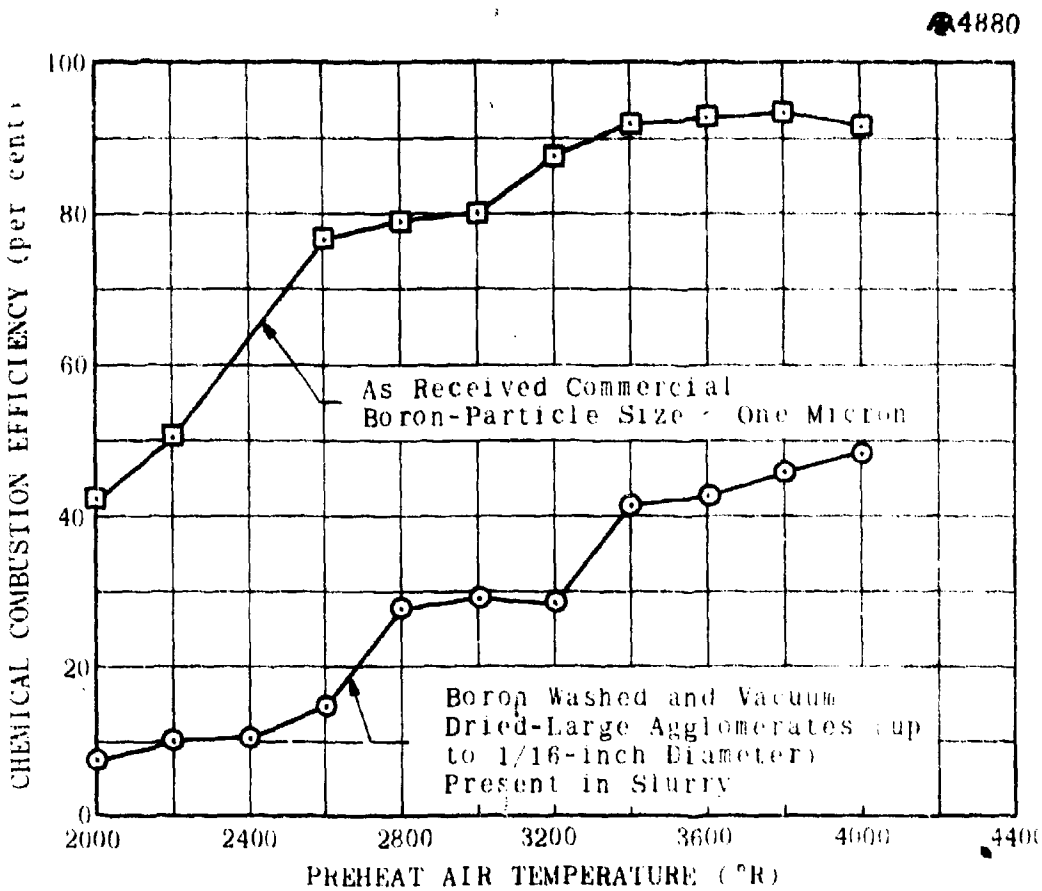

Figure 30. Effect of Agglomerate Size on Chemical Activity of Lightly Loaded (30% Solids) Boron-Isopropanol Slurries.

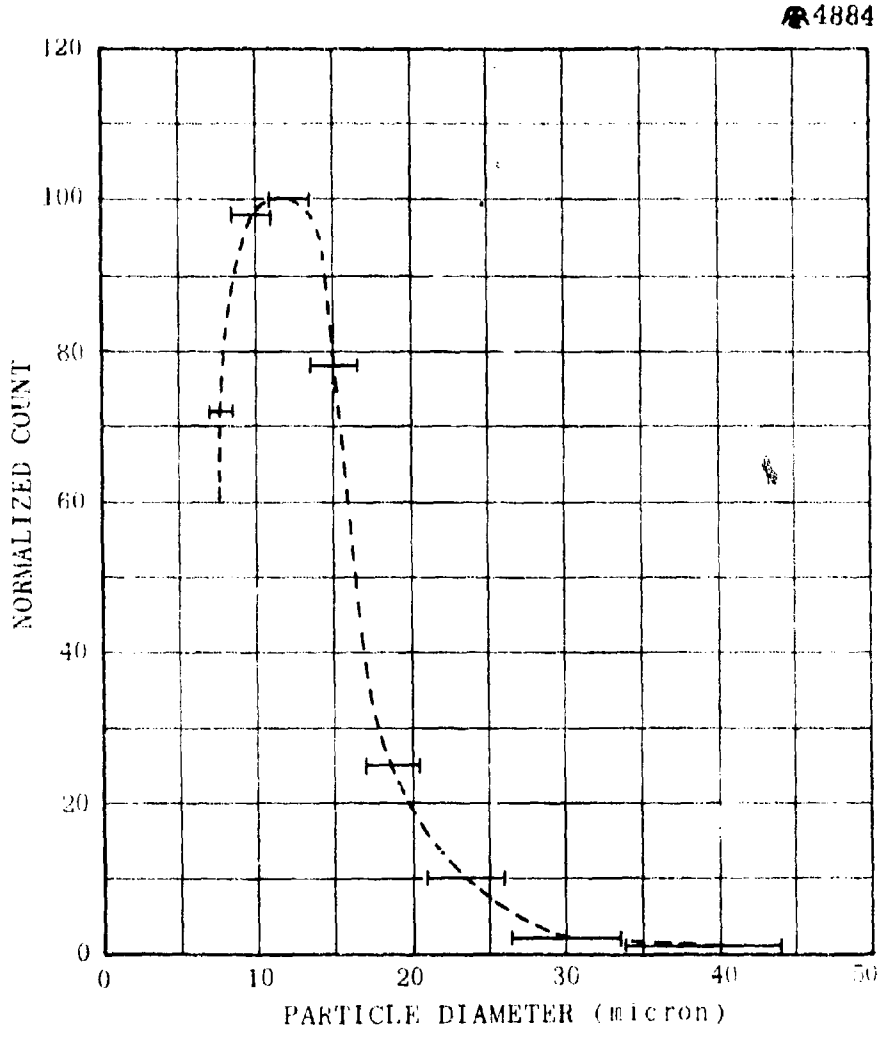

Figure 31. Coulter Counter Analysis of Boron Agglomerate Size in a Slurry of 50 Per Cent (Washed and Vacuum Dried) Commercial Boron and 50 Per Cent Isopropanol.

for several days and has not been shaken prior to removal of the Coulter sample. The particles counted by the Coulter Counter were, therefore, the smallest particles in the slurry.

A sample of the remaining vacuum-dried boron was dry ball-milled for thirty minutes in an attempt to reduce the size of the larger agglomerates. The resulting material was formulated into a slurry containing 75 per cent boron (solids), 22 per cent isopropanol, and three per cent surfactant (n-octyl amine). This slurry was fairly smooth and, although a rheogram was not determined because of the small amount of slurry available, it appeared much looser than slurries of similar loading made with dry ball-milled boron in isopropanol. Combustion results from the ambient pressure combustor showed that the slurry made with washed boron burned about as well as a similar slurry containing dry ball-milled boron, at the lower temperatures, as shown on Figure 32. At the higher temperatures the reduction in chemical activity is attributed to the presence of large agglomerates which three hours of ball-milling had not eliminated. These large particles were evident in the exhaust samples, and their size ranged up to about 1/32-inch in diameter as compared to 1/16-inch for the sample that had not been ball-milled. The combustion results for these isopropanol-based slurries are also compared with results for a 73 per cent boron slurry in JP-4 on Figure 32.

The results obtained thus far with the washed and dried boron slurries indicate that this method of processing may lend itself to close control of agglomerate particle size in slurries. This, with an accompanying improvement in loading and viscosity, may be possible to achieve at little or no loss in chemical activity.

4.1.6 Testing of Slurry Containing Blended Boron

The slurry made with a blend of commercial-grade and submicron boron described in Section 2.5, also was tested with the ambient pressure combustor. The results, compared with results for other slurries of similar solids loading, are presented on Figure 33. These data indicate

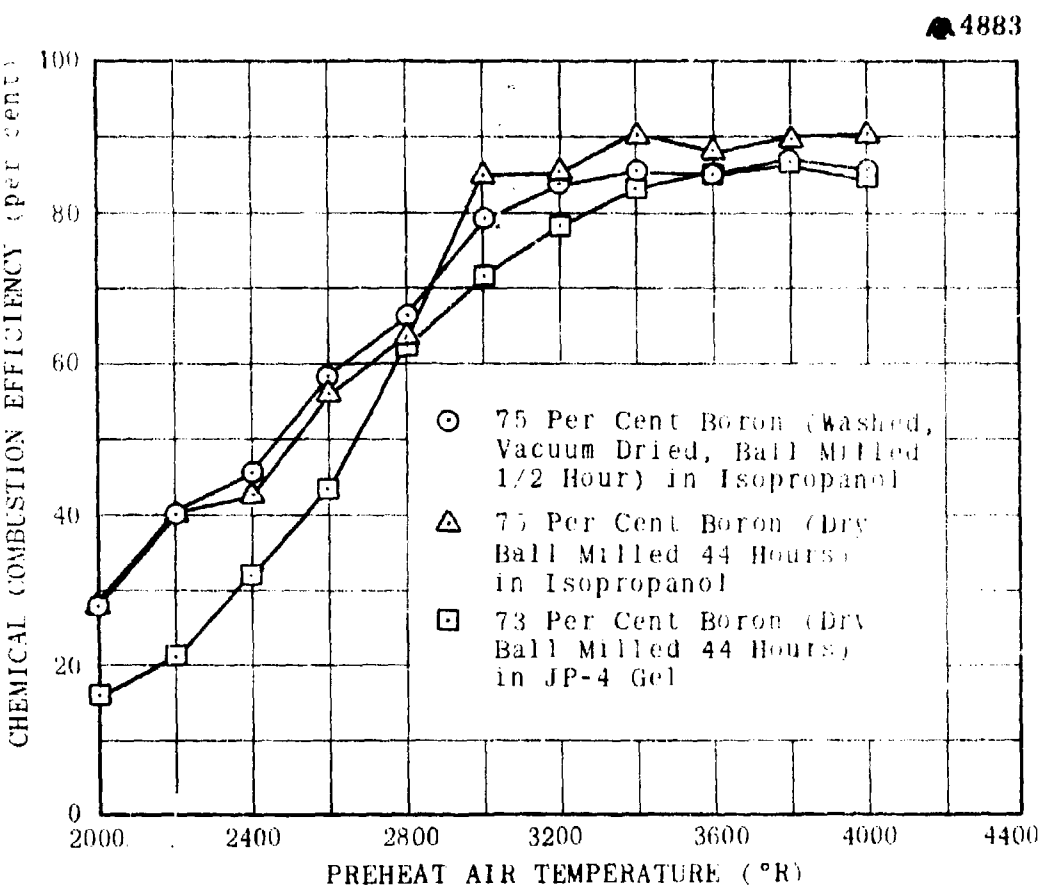

Figure 32. Comparison of Ambient Pressure Results for Three Types of Boron Slurry Formulations Containing Similar Solids Loadings.

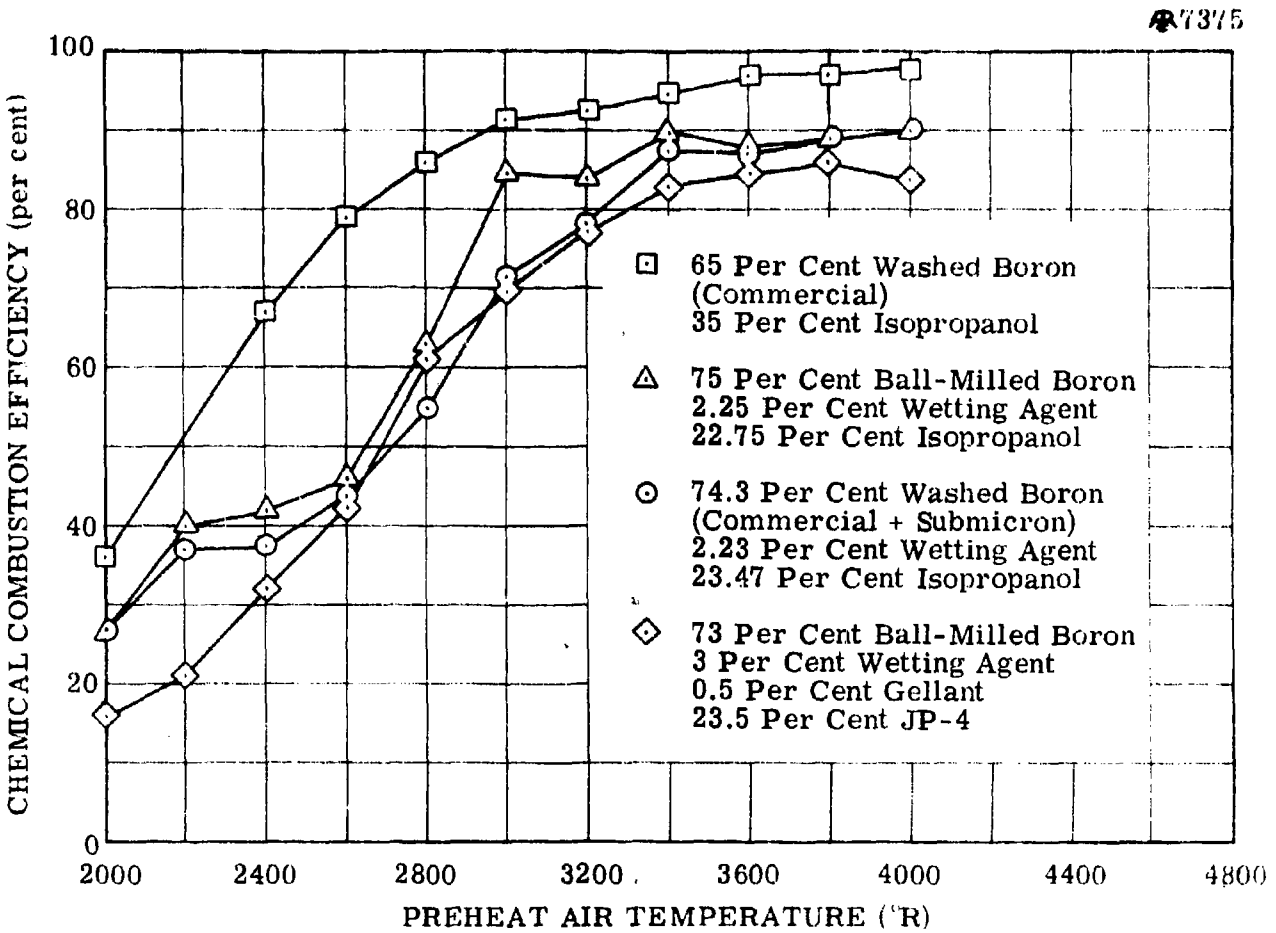

Figure 33. Comparison of Results from Ambient Pressure Combustion Tests of Bimodal (Commercial and Submicron) Washed Boron Slurry and Other Formulations.

that the slurry containing the blended boron was approximately equal in activity to the "standard" formulation of 75% ball-milled commercial boron in isopropanol, and was slightly more active than the slurry of 73 per cent ball-milled boron in gelled JP-4 (1964 "workhorse" formulation).

4.2 MICRO-RAMJET TEST EQUIPMENT

The equipment used in the micro-ramjet engine combustion tests with boron slurry fuels is described in the following paragraphs.

4.2.1 High Pressure Blowdown Facility

The air supply system for the micro-ramjet test engine consisted of air storage tankage, a compressor for pressurizing the storage tanks, a pebble bed heater used to heat the air, a mixing chamber for air temperature regulation, and associated piping and instrumentation. A photograph of the blow-down facility is presented as Figure 34. The air storage section consisted of twenty air-supply tanks (normally used for M14 torpedoes) of 130 cu ft capacity each. At a pressure of 2800 psig, approximately 5000 pounds of air can be stored in the tanks.

The pebble bed heater consisted of a brick-lined steel vessel filled with 3/8-inch diameter alumina pebbles. The bed was heated from the top by a removable propane torch to a temperature of about 5000°F at the top and 3000°F at the bottom. Cold and heated air were mixed just downstream of the outlet at the top of the pebble bed heater.

Total air flow rate and air temperature were measured downstream of the mixing section by a sonic venturi and bare-wire thermocouple, respectively. Maximum design air flow through the heater was ten pounds per second at 1000 psig pressurization. With this blow-down facility the condition of 600°F air at two pounds per second flow rate could be maintained for over fifteen minutes, or 330°F air at ten pounds per second for about five minutes.

4.2.2 Micro-Ramjet Engine Assembly

The air supply to the micro-ramjet engine from the blow-down facility passed through a knuckled pipe arrangement, about eight feet above

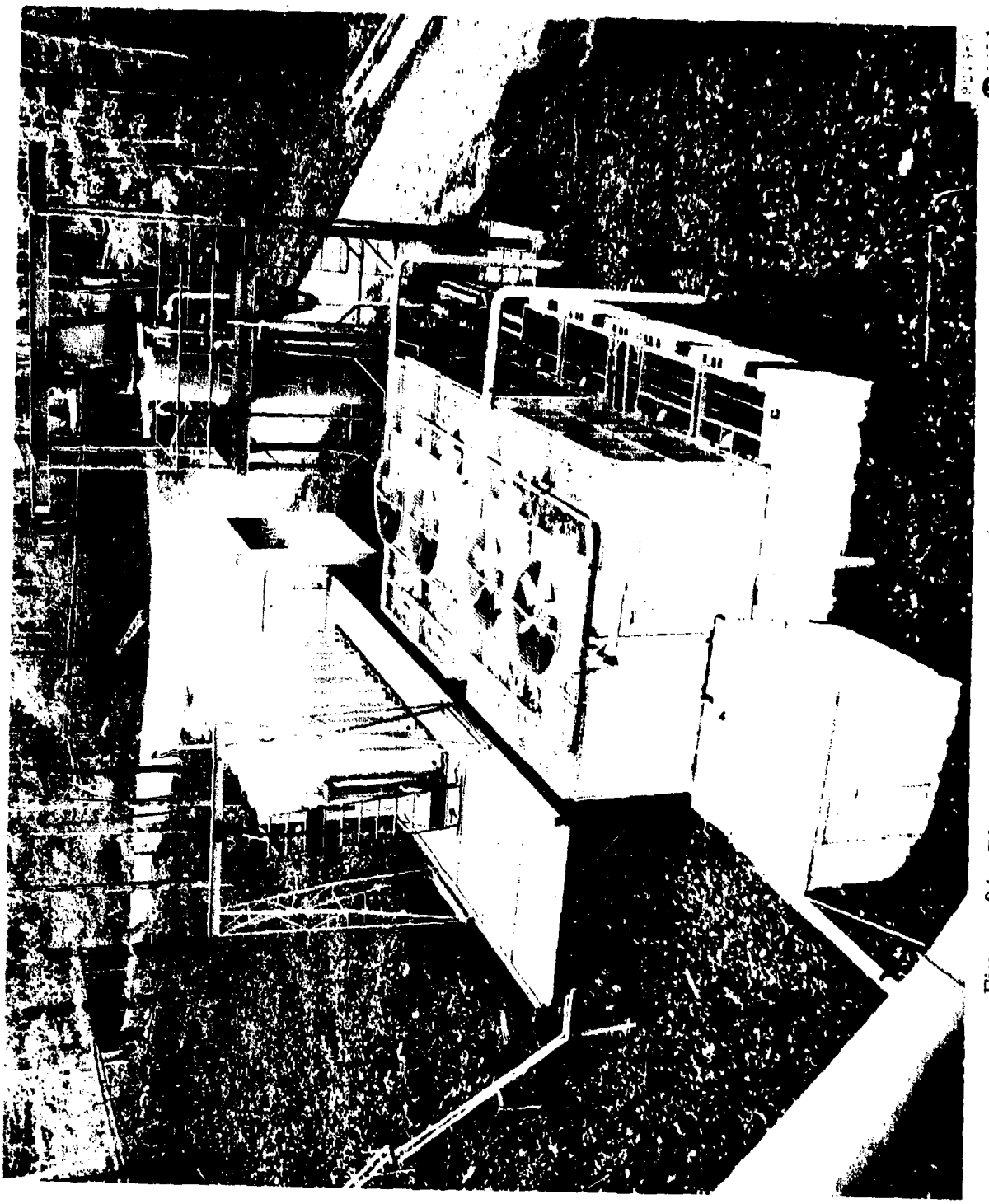

Figure 34. Photograph of the High Pressure Blow-Down Facility.

the engine assembly, in order to facilitate the measurement of delivered thrust. The preheated air entered a plenum forward of the engine and proceeded through a distributor section into the engine section. Three photographic views of the engine assembly are presented in Figures 35, 36, and 37.

The 3.5-inch ID engine assembly was segmented, as shown in Figure 35, in order to facilitate clean-up after the runs. The section in which the burner can was placed was equipped with a quartz window two inches in diameter, through which the combustion was photographed during each test. The entire engine assembly, including the nozzle section, was water-cooled.

4.2.3 Micro-Ramjet Accessories

4.2.3.1 Slurry Feed Ram

Slurry was injected with an electromechanical ram system (illustrated on Figure 37) which utilized a floating Teflon piston driven by a worm gear which in turn was driven by a one horsepower dc motor. The slurry flow rate was recorded as a proportional function of the rpm of the DC drive motor. A blowout disk rated at 800 lb/sq in was placed in the system to protect against buildup of excessive pressure on the ram.

4.2.3.2 Isokinetic Sampler

Exhaust products were sampled isokinetically by a water-cooled sampler head located about one inch downstream of the nozzle exit plane. The sampler was positioned at about one-third of the distance between the centerline of the nozzle and the outer diameter, in order to avoid particle sorting which was expected to be more likely at the center and the perimeter of the exhaust. The collected exhaust samples were quenched with water as they entered the sampler tube, and the suspended samples were then cooled in a heat exchanger and deposited in test tubes mounted in a circular positioner. Chemical analysis of the samples were performed similarly to those from the ambient pressure combustor tests[2].

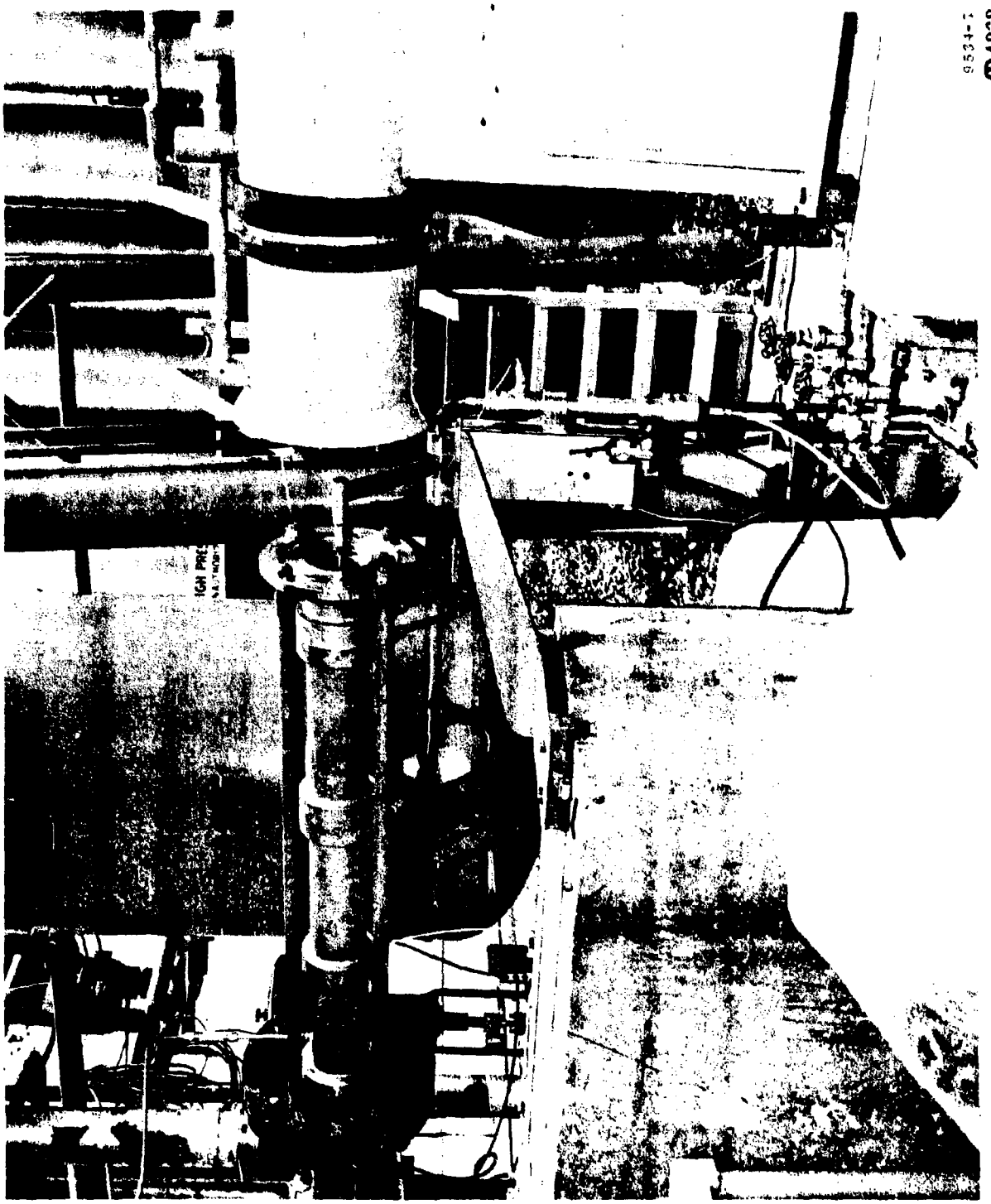

Figure 35 Photograph of Micro-Ramjet Engine Assembly Emphasizing the Segmented Burner Duct and the Isokinetic Sampler Assembly.

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Figure 36 Photograph of Micro-Ramjet Engine Assembly Emphasizing the Eductor System (at Left) and the Eductor Water Supply (Pump in Left Foreground).

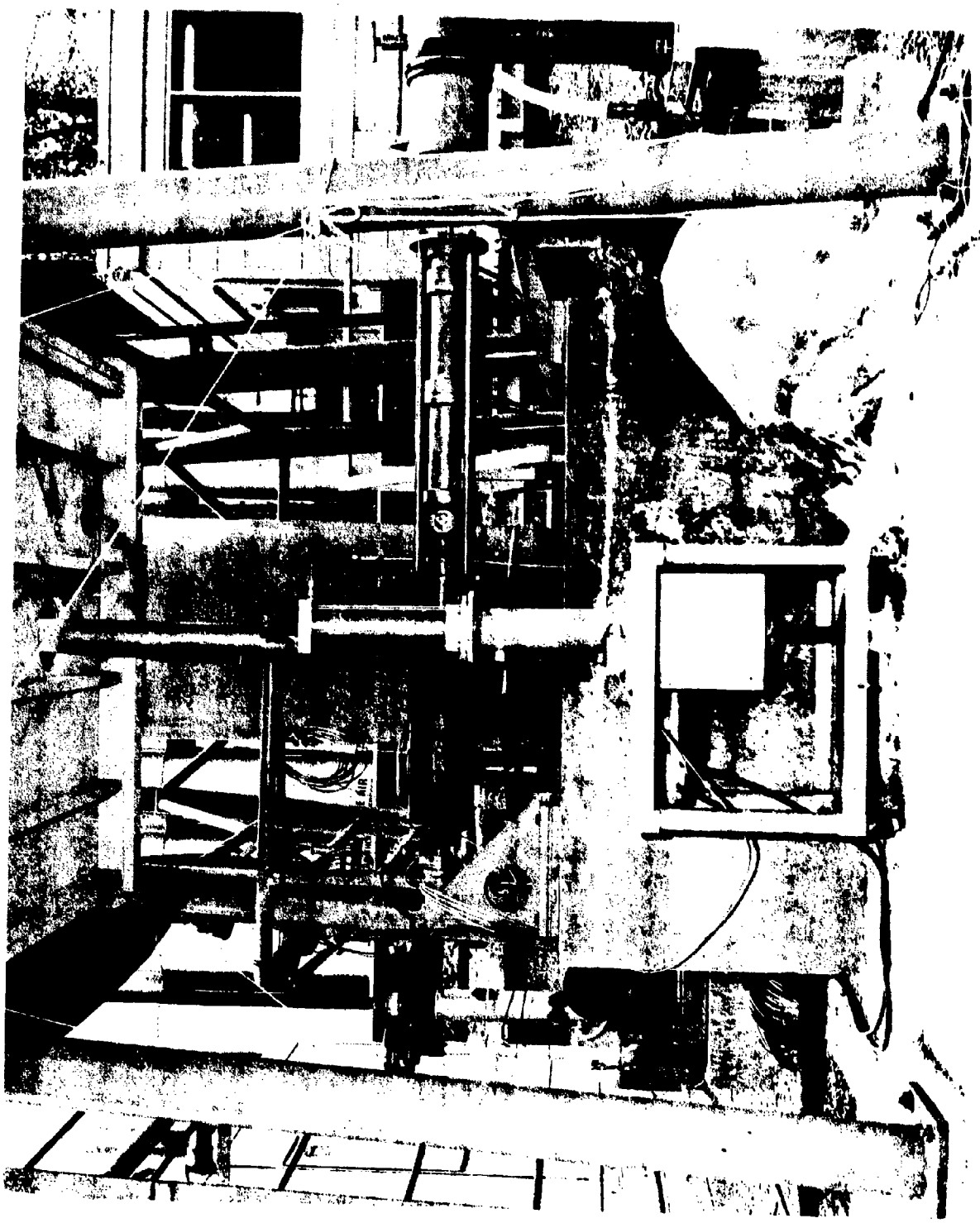

Figure 37. Photograph of Micro-Ramjet Engine Assembly Emphasizing Slurry Feed System in Center Foreground.

4.2.3.3 Total Pressure Rake

The five-point total-pressure rake constructed for use with the 3.5-inch micro-ramjet engine is shown on Figure 38. The pressure rake assembly was so constructed that water was purged through the pressure ports whenever data were not being recorded. The operation of the pressure data sampling system was coordinated with the isokinetic sampling system so that both operated over the same period of time.

4.2.3.4 Eductor System

The eductor system (shown on Figure 36) was used to water-quench the exhaust products and muffle the noise of testing. The exhaust products were removed from the test site to a distance of about fifty feet. A large underground septic tank was provided for storage of condensed exhaust products, and noncondensibles were exhausted to the atmosphere through a stack twelve feet in height.

4.2.3.5 Particle Mill and Burner Can

The particle-mill burner-can combination used in these tests was scaled from the Marquardt 8A configuration used in 1964[2,7]. This design, illustrated on Figure 39, allowed approximately ten per cent of the air entering the combustion process to pass through the particle mill, where it atomized incoming fuel by means of a rotational momentum component imparted by the radial vanes, shown at the top of Figure 39. Ignition was effected with a hydrogen-oxygen torch which was placed just forward of the burner can skirt (pierced section).

After burnthroughs occurred in the first series of slurry tests, a 0.03-inch coating of zirconia was flame-sprayed onto the interior of the skirt of the burner cans. While the zirconia did not completely eliminate pitting with some attendant increase in air flow area, it did allow each can to be used for three or four tests instead of only one.

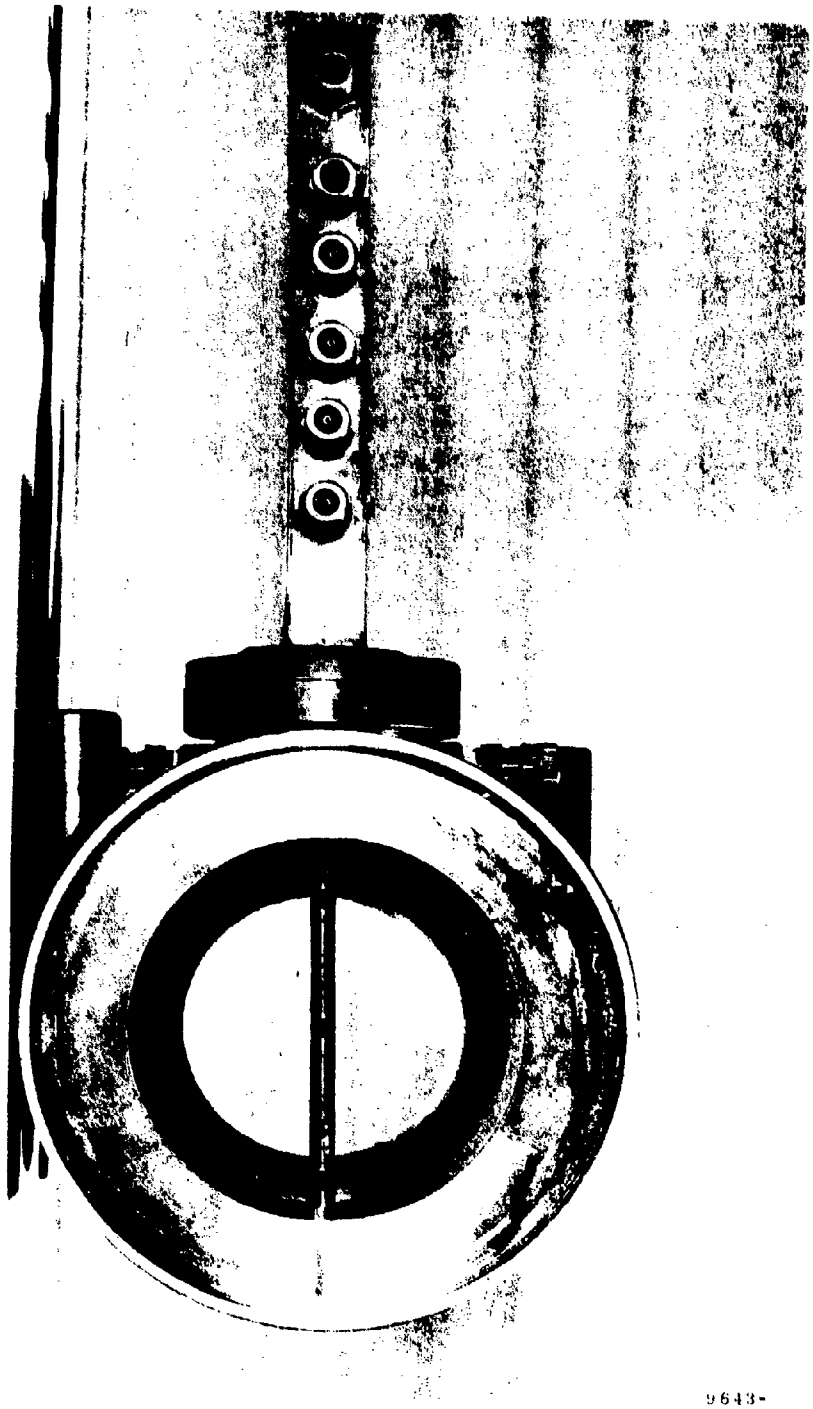

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Figure 38. Photograph of Five-Point Pressure Rake used with the 3.5-inch Micro-Ramjet Engine (Rake Shown Installed in Nozzle Housing).

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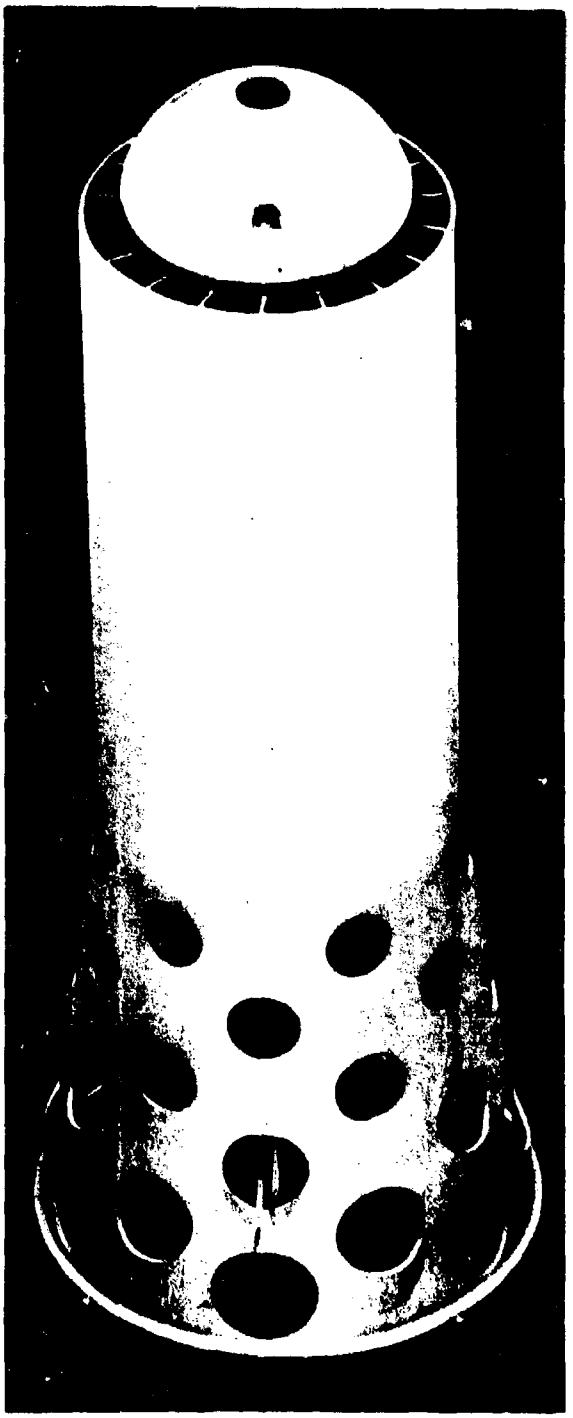

Figure 39 Photograph of Particle Mill and Burner Can Section for 3.5-inch Micro-Ramjet Test Engine.

4.2.3.6 Dual Fluid Injector

The dual fluid injector for the micro-ramjet engine was designed to fit into a modified test section which could include any burner can design used with the injector. Injector air supply and slurry feed lines were incorporated into the injector assembly, and both entered the test section through the assembly fitting at the top of the injector shown on Figure 40. In this figure, the dual fluid injector is shown in a cold flow test. The particles emerging from the injector are very small, and can hardly be distinguished from the background of the photograph.

The injector air, taken from the main air supply, entered at a temperature slightly above ambient, and the pressure was controlled between zero and 500 lb/sq in by a valve actuated from the control house. A slight swirl was imparted to the injector air to promote turbulence at the air-slurry interface. The swirling air stream issued from a narrow annular gap (0.001 to 0.010 inches wide) and impinged perpendicularly onto the slurry stream. The atomization appeared very uniform, and no problems in maintaining regularity or the cone angle of the resulting slurry spray were encountered.

Various types of burner-can configurations were used with the dual fluid injector. These will be discussed later in connection with the specific tests in which they were used.

4.3 TEST PROCEDURES AND DATA REDUCTION

4.3.1 Data Recording

All data pertinent to each test were recorded on an eighteen-channel recording oscillograph. This information included: venturi pressures and temperatures for calculating air mass flow and inlet conditions; rpm of slurry ram feed; cooling water flow rate and temperatures; chamber pressure; thrust; and total and static pressures from the pressure rake. In addition, the sequencing of the exhaust sample collection (and pressure rake measurements, when applicable) was recorded on the chart. Each three-

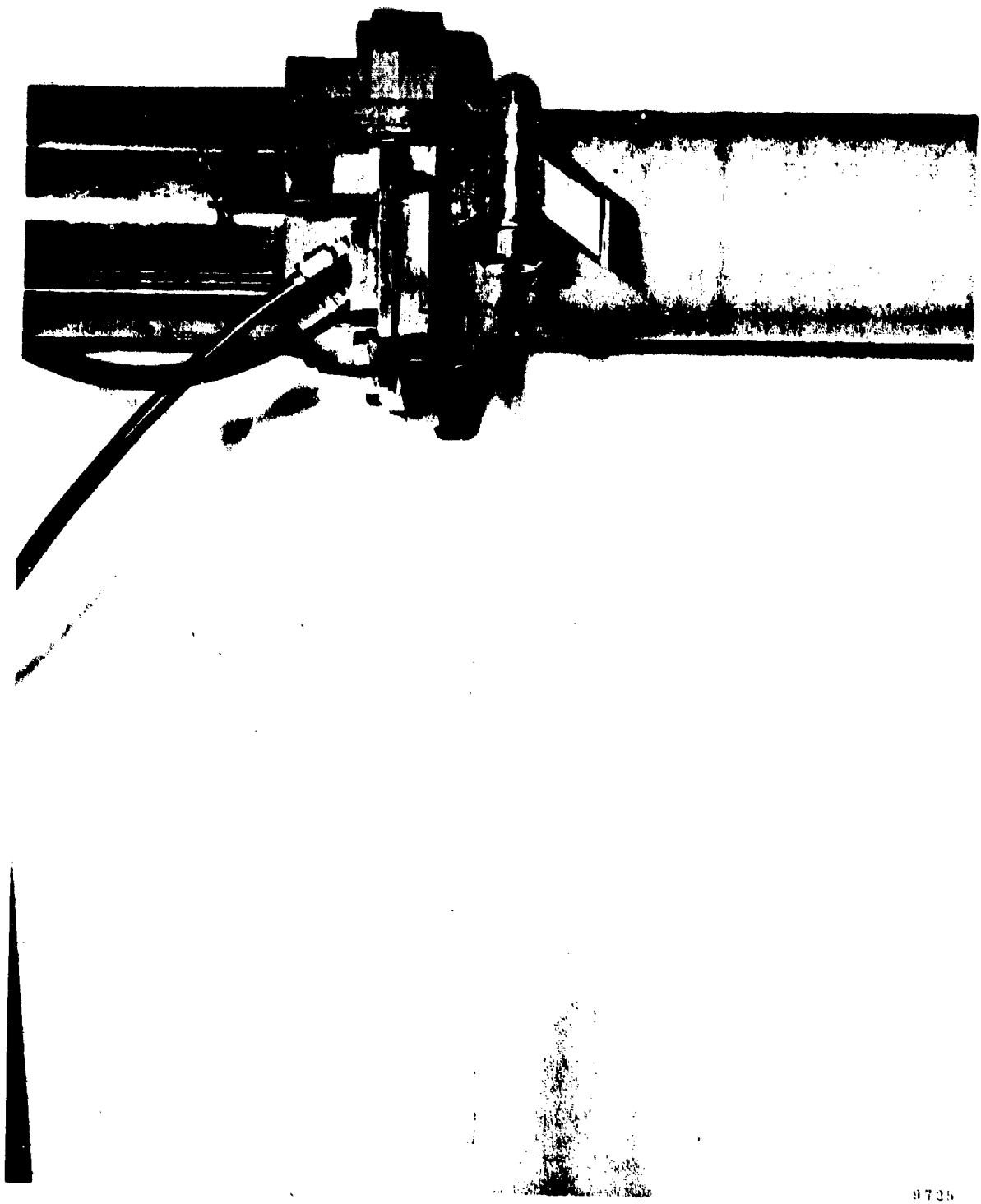

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Figure 40. Photograph of Dual-Fluid Injector Designed for Use with the 3.5-inch Micro-Ramjet Engine, under Cold Flow Conditions with a Slurry of 73 Per Cent Boron in JP-4.

second period of exhaust product sampling corresponded to each of the various slurry feed rates (fuel-to-air ratios) used, in order that data points from chemical analysis of the exhaust, thrust measurement, and total pressure measurements represented the same period of operating time.

Motion pictures were taken of the exhaust and through the viewing port in the test section for almost all of the tests. Close visual observation of the tests also was very important, since the relative size of the particles in the exhaust prior to ignition could indicate whether the atomization was effective, and successful ignition could also be determined visually. In addition, loss of fuel feed (rupture of blowout disc) or loss of cooling water could be verified by visual observation.

4.3.2 Test Procedures

After pressurization of the air storage tanks, heating of the pebble bed, and assembly of the engine components, the tests proceeded as follows:

(1) Check out and calibrate all transducers
(2) Position cameras
(3) Position and check out exhaust sample collector mechanism
(4) Bring slurry up to the combustion chamber inlet
(5) Start and set water flow (for chamber cooling and eductor)
(6) Bring inlet conditions to desired settings (low mass flow for ignition)
(7) Begin slurry flow
(8) Ignite hydrogen pilot (igniter)
(9) When slurry is ignited, bring fuel feed rate and air flow rate to test conditions.
(10) Initiate cameras and position sampler head
(11) Shut off igniter
(12) Step through programmed values of slurry feed rate, taking an exhaust sample for each value
(13) Shut down air, water, etc., and secure facility.

When the hydrogen pilot was ignited the slurry flow had not reached the atomizer. Thus, the slurry was ignited at an unknown fuel-to-air ratio corresponding to a transient inlet air condition.

This general procedure was followed for all of the tests reported herein. When the dual-fluid injector was used, injector air pressure was set shortly before ignition. When the pressure rake was used, the control button for the sampler points also actuated the total pressure sensing system. A number of tests were aborted, usually because of rheological difficulties with the fuel. In these cases, the blow out diaphragm would rupture, sending slurry down a clear plastic tube visible from the control house. In this manner the order for abortion could be signalled quickly in order to conserve slurry.

4.3.3 Data Reduction

The chemical analyses of the exhaust products, described fully in Reference 2, resulted in chemical combustion efficiencies of the boron in the fuel. These values were directly comparable to the values derived from thrust, since the samples were obtained simultaneously with the thrust trace for each value of fuel-to-air ratio.

A computer program was written to aid in the calculation of combustion efficiencies and other data from measured values of thrust. The basis of the program is included as Appendix II of this report.

The total pressure data obtained from the three pressure-rake tests were reduced to values of combustion efficiency by The Marquardt Corporation. The computer program used to reduce pressure data from previous Marquardt ramjet combustion tests was used to process the total pressure data from this series of tests.

4.4 RESULTS OF BASE-LINE COMBUSTION TESTS (PARTICLE-MILL INJECTION)

The purpose of this portion of the combustion testing was to establish a comparison between combustion performance of boron slurries in the 3.5-inch micro-ramjet and their performance in the 6.3-inch ramjet

used by Marquardt for previous slurry combustion testing[7]. Slurry formulations other than those previously tested by Marquardt were also tested in the micro-ramjet in order to determine their relative performance.

4.4.1 Check-Out and Calibration Tests

Several bare-duct (no burner can present, no slurry flow) tests were performed prior to the main test series to check out system functions and to check the calibration of the load cell and the venturi system for determining inlet air conditions. Another test was run, with the burner can present, in which SO_2-extracted paraffinic kerosene (approximately C_{12} hydrocarbon) was burned. This fuel did not burn well, and stable combustion was never achieved.

Other check-out tests included in the base-line combustion series are described on Table XIX. The results of test No. 8 indicated that no change in thrust was caused by the placement of the isokinetic sampler head in the exhaust of the engine. The results of test No. 9 verified that a parallelogram loading device inserted between the face of the air distribution plenum and the load cell prevented side loading on the load cell due to thermal expansion of assembly components. Although side loading appeared to be only a minor problem in the early runs, it was believed that in several tests sudden changes in thrust could be attributed to slipping of the plenum-load cell contact face due to thermal growth of the air delivery duct.

4.4.2 Test Conditions

The nominal test conditions for the base-line series were as follows:

(a) Mach 2.5 at sea level
(b) Air flow rate: 8.7 lb/sec at 440°F
(c) Chamber pressure: 125 to 150 psia
(d) Fuel-to-air ratio: 0.005 to 0.02
(e) Total combustion volume: 41.25 cu in; duct diameter 3.5 in
(f) Nozzle (A_5/A_4): 0.60
(g) Fraction of inlet air passing through particle mill approximately 10 per cent.

TABLE XIX

CHECK-OUT TESTS PERFORMED WITH THE 3.5-INCH MICRO-RAMJET TEST ENGINE AS A PART OF THE BASE-LINE COMBUSTION TEST SERIES

Test No.	Purpose	Type
8	To determine effect of isokinetic sampler head insertion on measured thrust; also, to provide further bare-duct calibration	Bare-duct (no burner can; no combustion)
9	To evaluate device to eliminate side loading on the load cell; and to provide further calibration	Bare-duct (no burner can; no combustion)
10	To evaluate the drag characteristics of the particle mill-burner can assembly	Burner can installed; no combustion
11	To obtain a bare-duct calibration of the test apparatus with the pressure rake equipment installed.	Bare-duct (no burner can; no combustion)

The combustor volume was measured from the exit of the particle mill to the exit plane of the nozzle.

In all of the base-line tests the temperature of the slurry was ambient, which varied from 55°F to 90°F.

4.4.3 Test Results

The slurry formulation used and the general results for each micro-ramjet test in the base-line series are presented on Tables XX and XXI. The series of tests described on Table XXI included the total pressure rake as a third method of determining fuel performance.

The results of Tests 1 through 7 are tabulated in Tables XXXII through XLIII of Appendix III. Plots of the data in terms of combustion efficiency versus fuel-to-air ratio are presented in Figure 41 through 46, and the micro-ramjet data are compared with Marquardt data[7] for the 6.3-inch ramjet for the three slurries tested in the Marquardt engine. Plots of combustion efficiency versus equivalence ratio for most of the tests are presented in Figures 71 through 74 in Appendix III.

In Figures 41 through 46, the chemical combustion efficiency of the boron (determined from exhaust sampling) was taken to be that of the entire slurry. It was found that the assumption of complete carrier combustion was not valid for these fuels. The deviations which occurred between the assumption of complete carrier combustion and carrier combustion efficiency equal to that of the boron are indicated on Tables XXXII through XLIII of Appendix III.

It should be noted that no test data could be obtained with the isooctane-based slurry in test No. 5 because of rheological difficulties. Rheological problems were also observed with the slurry of 65 per cent washed boron in isopropanol (Test No. 7) at a shear rate of about 300 sec^{-1}. The latter flow stoppage was believed due to inhomogeneities in the slurry resulting from inadequate mixing, and not to dilatancy of the slurry at the shear rate attained.

TABLE XX

SUMMARY OF SLURRY FORMULATIONS AND GENERAL COMMENTS FOR MICRO-RAMJET TESTS WITH PARTICLE MILL INJECTION

Test No.	Formulation	General Test Results
1	73.0% Ball Milled Boron 2.19% Glycerol Sorbitan Laurate 24.07% JP-4 0.74% Aluminum Soap	(a) No System Problems (b) Good Combustion (c) Burner Can Failed (d) Burnthrough in Water Jacket
2	64% Ball Milled Boron 16% $B_{13}P_2$ 2.4% Glycerol Sorbitan Laurate 17.34% SO_2-Extracted Paraffinic Kerosene 0.26% Polystyrene Gellant	(a) No System Problems (b) Much Unburned Slurry in Exhaust (c) Heavy Deposition in Combustor
3	75% Ball Milled Boron 1.88% Amine Surfactant 23.12% Isopropanol	(a) No System Problems (b) Good Combustion (c) Burner Can Failed
4	70% Ball Milled Ultra-Fine, High Purity Boron 28.8% JP-4 4.2% Glycerol Sorbitan Laurate	(a) No System Problems (b) Good Combustion (c) Burner Can Failed
5	80% Ball Milled Boron 2.4% Glycerol Sorbitan Laurate 0.53% Polystyrene Gellant 17.07% Isooctane	(a) Fuel Plugged in each of Three Test Attempts (b) Ignition Achieved Twice, But No Data
6	75% Ball-Milled Submicron Boron 20.5% JP-4 4.5% Glycerol Sorbitan Laurate	(a) No System Problems (b) Poor Combustion (c) Few Burnthrough Holes in Burner Can
7	65% Isopropanol-Washed Boron 35% Isopropanol	(a) Fuel Stoppage at Third Data Point (b) Little Deposition in Combustor (c) Burner Can Failed (d) Excellent Combustion

TABLE XXI

QUALITATIVE RESULTS OF BASE-LINE COMBUSTION TESTS IN THE 3.5-INCH MICRO-RAMJET ENGINE EQUIPPED WITH A FIVE-POINT TOTAL PRESSURE RAKE

Test No.	Slurry Formulation	Nominal Air Inlet Conditions	Results and Observations
12	73% Boron 23.82% JP-4 0.99% Polystyrene Gellant 2.19% Glycerol Sorbitan Laurate	Mach. 2.5 at Sea Level, Cold Day	Good combustion, but no thrust or pressure data due to reorder malfunction; burner can and rake intact.
13	(Same as 12)	(Same as 12)	Fair to good combustion; burner can and rake intact.
14	75% Boron 23.12% Isopropanol 1.88% Amine Surfactant	(Same as 12)	Good combustion; few pits in burner can; rake intact.
15	80% Boron 17.07% Isooctane 0.53% Polystyrene Gellant 2.4% Glycerol Sorbitan Laurate	(Same as 12)	Good combustion, but fuel became dilatant on third point; flow rate was dropped and increased for four more points. Very heavy deposition on can.

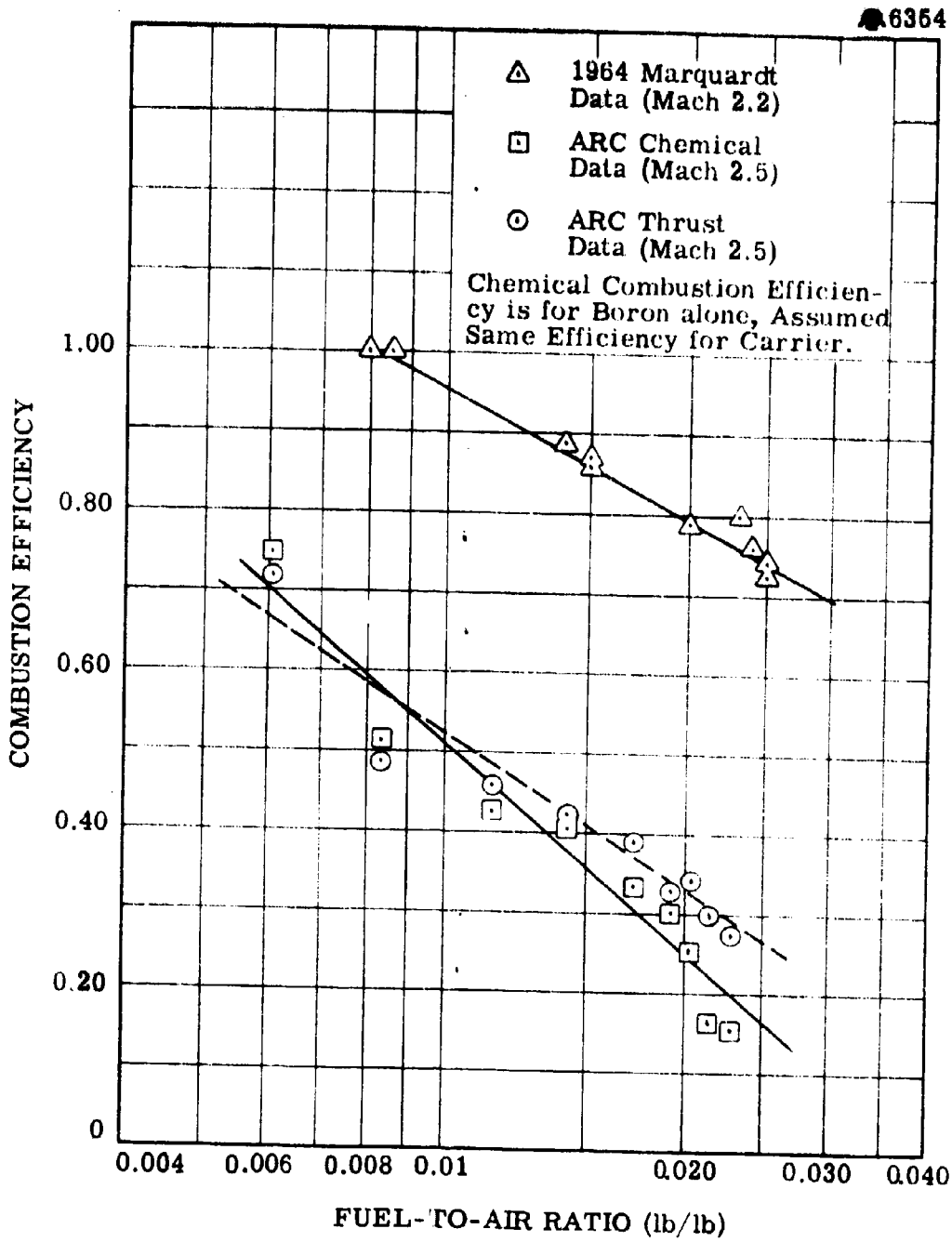

Figure 41. Comparison of ARC Micro-Ramjet Data, from Exhaust Sampling and Thrust Measurement in 3.5-inch Micro-Ramjet using Particle Mill, and 1964 Marquardt Results in 6.3-inch Test Engine, for Slurry of 73 Per Cent Boron in JP-4. ARC Conditions - Mach 2.5, Sea Level; Marquardt Conditions - Mach 2.2, Sea Level.

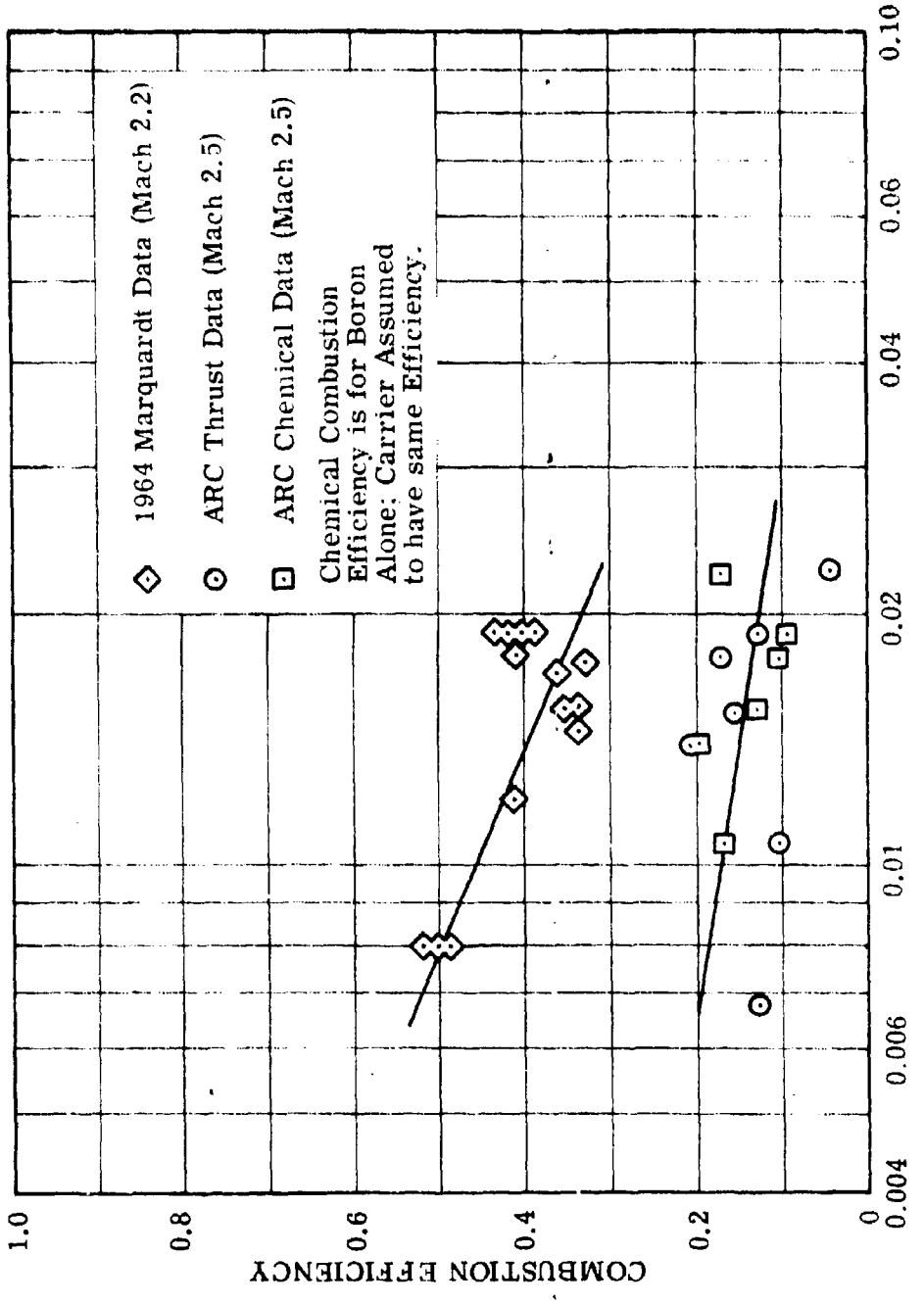

Figure 42. Comparison of ARC Micro-Ramjet Data, from Exhaust Sampling and Thrust Measurement in 3.5-inch Test Engine Using Particle Mill, and 1964 Marquardt Results in 6.3-inch Test Engine, for Slurry of 64 Per Cent Boron, 16 Per Cent $B_{13}P_2$ in SO_2-Extracted Paraffinic Kerosene, ARC Conditions - Mach 2.5 at Sea Level; Marquardt Conditions - Mach 2.2 at Sea Level.

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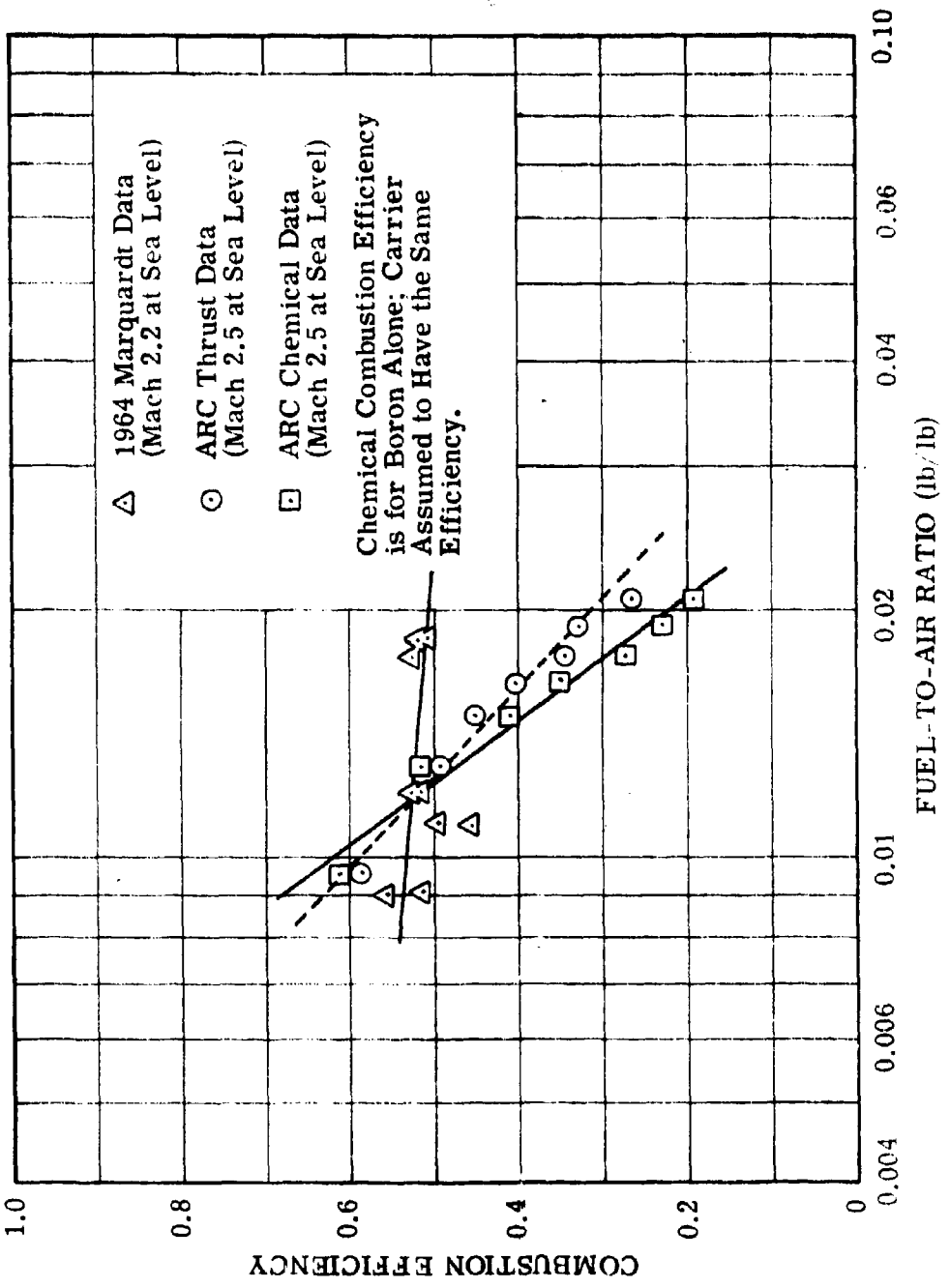

Figure 43. Comparison of ARC Micro-Ramjet Data from Chemical Sampling of Exhaust and Thrust Measurement in 3.5-inch Test Engine Using Particle Mill, and 1964 Marquardt Data from 6.3-inch Test Engine, for Slurry of 75 Per Cent Boron in Isopropanol.

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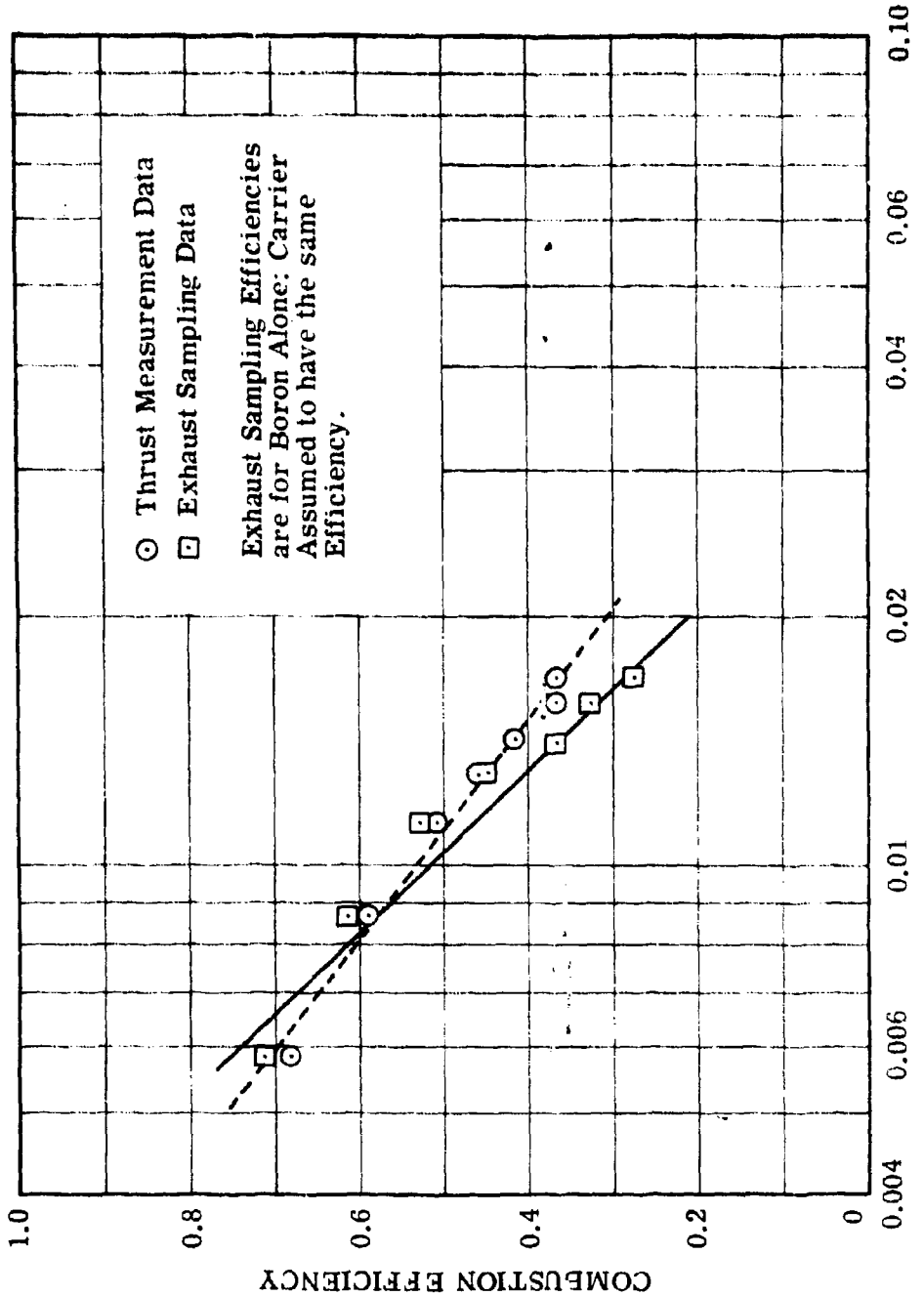

Figure 44. Comparison of Data from Chemical Sampling of Exhaust with Data from Thrust Measurement for Slurry of 70 Per Cent High Purity, Ultra-Fine Boron in JP-4, Tested in 3.5-inch ARC Micro-Ramjet Test Engine. Inlet Conditions - Mach 2.5 at Sea Level.

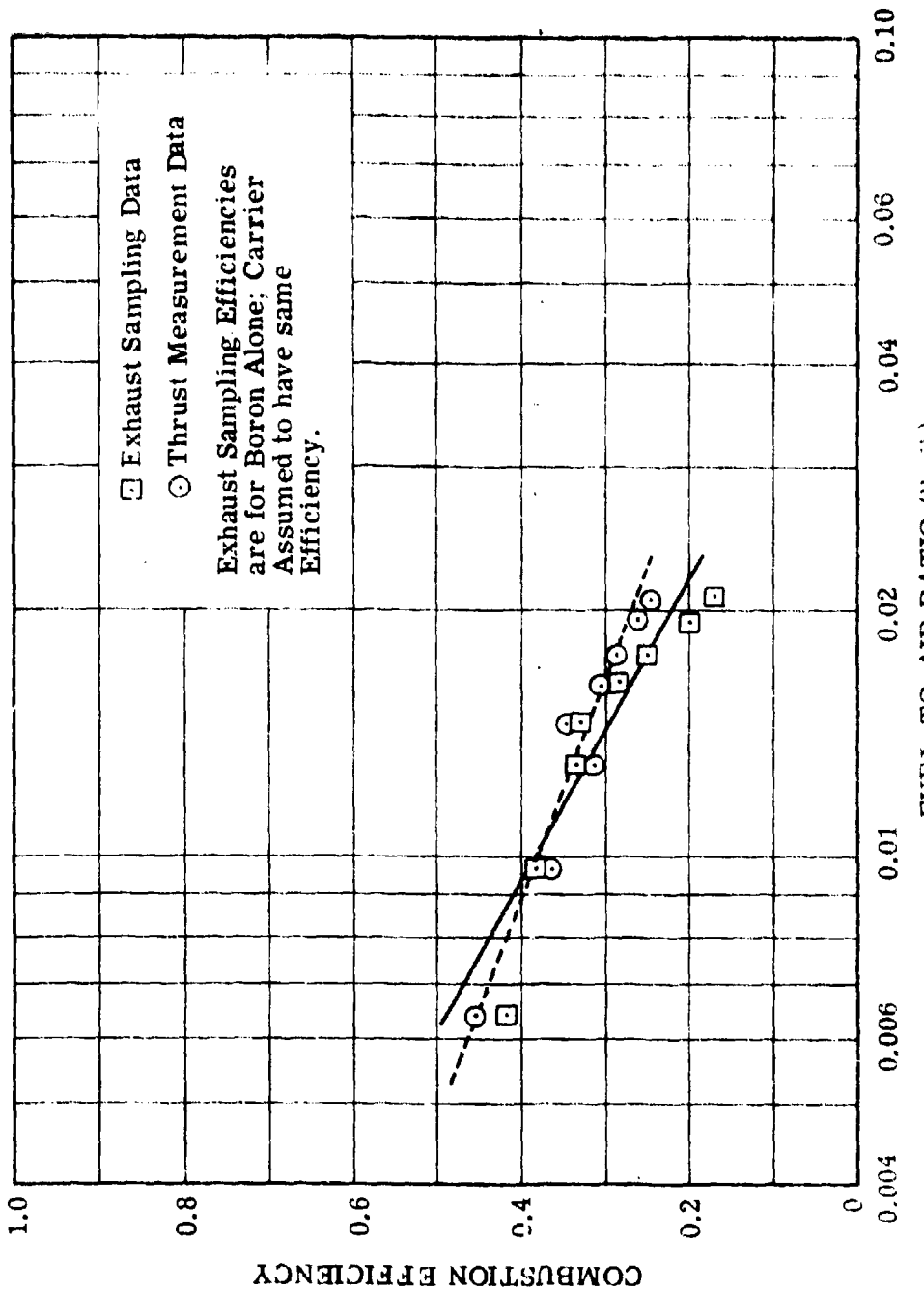

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Figure 45. Comparison of Data from Chemical Sampling of Exhaust and Thrust Measurements for Slurry of 75 Per Cent Submicron Boron in JP-4, Tested in 3.5-inch ARC Micro-Ramjet Test Engine. Inlet Conditions - Mach 2.5 at Sea Level.

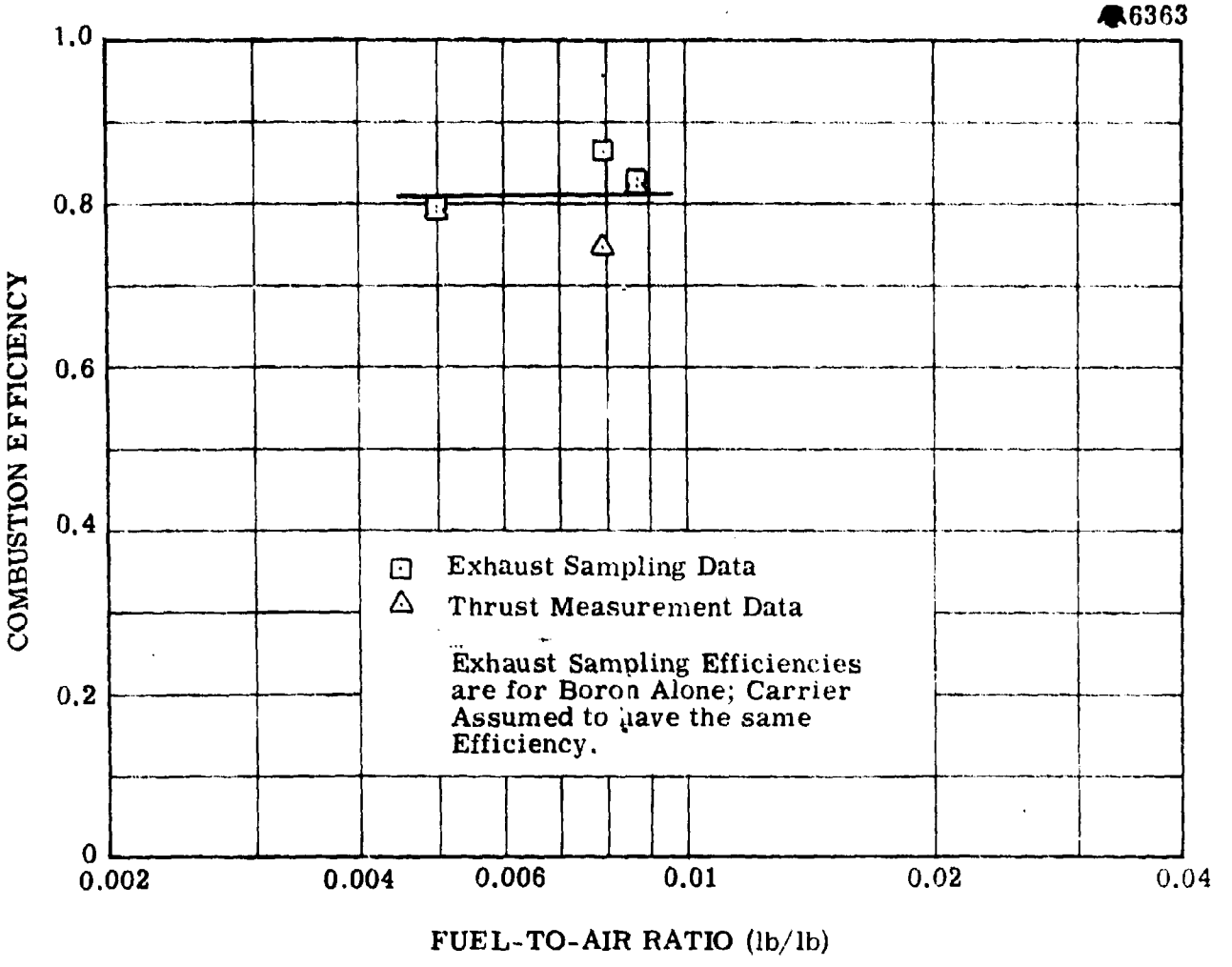

Figure 46. Comparison of Data from Chemical Sampling of Exhaust and Thrust Measurements for Slurry of 65 Per Cent Washed Boron in Isopropanol, Tested in 3.5-inch ARC Micro-Ramjet Test Engine. Inlet Conditions - Mach 2.5 at Sea Level.

Tests 12 through 15 utilized the five-point total pressure rake to determine slurry performance, in addition to thrust measurement and chemical analysis of exhaust sampling. The results of the tests with the pressure rake are compared on Tables XXII, XXIII, and XXIV to other tests without the rake installed. Total pressure data from the rake are presented on Tables XLV, XLVII, and XLIX in Appendix III. Combustion efficiencies from these tests are plotted as a function of equivalence ratio on Figures 75, 76, and 77 of Appendix III.

The procedure of Test 15 for the isooctane-based slurry was altered from that usually followed because the slurry proved to be dilatant at a fuel-to-air ratio of about 0.013 (or a fuel flow rate of about 1.12 lb/sec), and higher fuel flow rates could not be obtained. This value of f/a corresponds to a shear rate of about 400 sec^{-1} through the slurry feed line. It is not surprising that the slurry of 80 per cent boron in isooctane was dilatant at these shear rates, but it was believed that the available pressure of 800 psi would have been sufficient to deliver flow at shear rates higher than 400 sec^{-1}.

4.4.3 Discussion of Results

4.4.4.1 General

A summary plot of all of the micro-ramjet tests which utilized particle-mill injection is presented on Figure 47. Three of the fuels performed in the shaded band, indicating that their performance for the configuration and conditions used was similar. Since two of the fuels in this band were "standard" formulations (73 per cent boron in JP-4; 75 per cent boron in isopropanol), the performance of these fuels may be used as a standard to compare the properties of the other fuels tested, and to list some possible reasons why their performance deviated from the standard. This comparison, and the relative ranking of the fuels as to combustion efficiency, is presented on Table XXV. Table XXV also includes a relative ranking of the slurries based on heat released per unit volume at a fuel-to-air ratio of 0.01.

According to Table XXV, it appears likely that deviations from the "standard" of performance were caused by differences in particle size resulting from atomization and differences in the relative volatility of the carrier. There is also a possibility that elimination of surface contamination (through washing, in this case) can enhance combustion performance.

TABLE XXII

RESULTS OF COMBUSTION TESTS OF JP-4 BASED BORON SLURRIES CONTAINING 73 PER CENT SOLIDS, TESTED IN THE 3.5-INCH MICRO-RAMJET ENGINE WITH AND WITHOUT THE TOTAL PRESSURE RAKE (INLET CONDITIONS - MACH 2.5 AT SEA LEVEL, COLD DAY)

Combustion Efficiencies[a]

Fuel-to-Air Ratio lb/lb	Test 1[b] Exhaust Samples	Test 1[b] Thrust	Test 12[b] Exhaust Samples	Test 13[b] Exhaust Samples	Test 13[b] Thrust	Test 13[b] Total Pressure[c]
0.0060	0.75	0.72	0.79	0.63	0.53	42.8
0.0083	0.51	0.49	0.60	0.69	0.59	50.6
0.0115	0.43	0.46	0.54	0.54	0.45	43.0
0.0142	0.40	0.42	0.47	0.45	0.43	40.1
0.0.62	0.34	0.39	0.42	0.41	0.41	39.6
0.0193	0.30	0.33	0.41	0.30	0.38	37.9

a. The "Exhaust Sample" combustion efficiencies are for boron alone.

b. The slurry in Test 1 contained 0.74 per cent aluminum soap gellant; The slurry in Tests 12 and 13 contained 0.99 per cent modified polystyrene gellant. The pressure rake was installed in tests 12 and 13.

c. Data reduced by The Marquardt Corporation.

TABLE XXIII

RESULTS OF COMBUSTION TESTS OF AN ISOPROPANOL-BASED BORON SLURRY CONTAINING 75 PER CENT SOLIDS, TESTED IN THE 3.5-INCH MICRO-RAMJET ENGINE WITH AND WITHOUT THE TOTAL PRESSURE RAKE (INLET CONDITIONS - MACH 2.5 AT SEA LEVEL, COLD DAY)

	Combustion Efficiencies[a]				
	Test 3[b]		Test 14[b]		
Fuel-to-Air Ratio	Exhaust Samples	Thrust	Exhaust Samples	Thrust	Total Pressure[c]
0.0061	--	--	0.76	0.39	32.6
0.0096	0.62	0.59	0.76	0.49	52.2
0.0129	0.52	0.49	0.72	0.45	48.9
0.0149	0.41	0.45	0.65	0.39	44.1
0.0192	0.23	0.33	0.52	0.33	41.4
0.0207	0.19	0.27	0.45	0.27	37.3

a. The "Exhaust Sample" combustion efficiencies are for boron alone.

b. Test 14 was with the pressure rake installed; Test 3 was without the rake

c. Data reduced by The Marquardt Corporation.

TABLE XXIV

RESULTS OF COMBUSTION TEST OF AN ISOOCTANE-BASED BORON SLURRY CONTAINING 80 PER CENT SOLIDS, TESTED IN THE 3.5-INCH MICRO-RAMJET ENGINE EQUIPPED WITH THE TOTAL PRESSURE RAKE (INLET CONDITIONS - MACH 2.5, SEA LEVEL, COLD DAY)

Approximate Fuel-to-Air Ratio lb/lb	Combustion Efficiencies		
	Exhaust Samples[a]	Thrust	Total Pressure[b]
0.0033	0.67	0.68	50.5
0.0049	0.73	0.69	63.5
0.0060	0.82	0.75	57.5
0.0064	0.79	0.78	71.1
0.0081	--	0.75	67.3
0.0097	0.77	0.69	48.6

a. The "Exhaust Samples" combustion efficiencies are for boron alone.

b. Data reduced by The Marquardt Corporation.

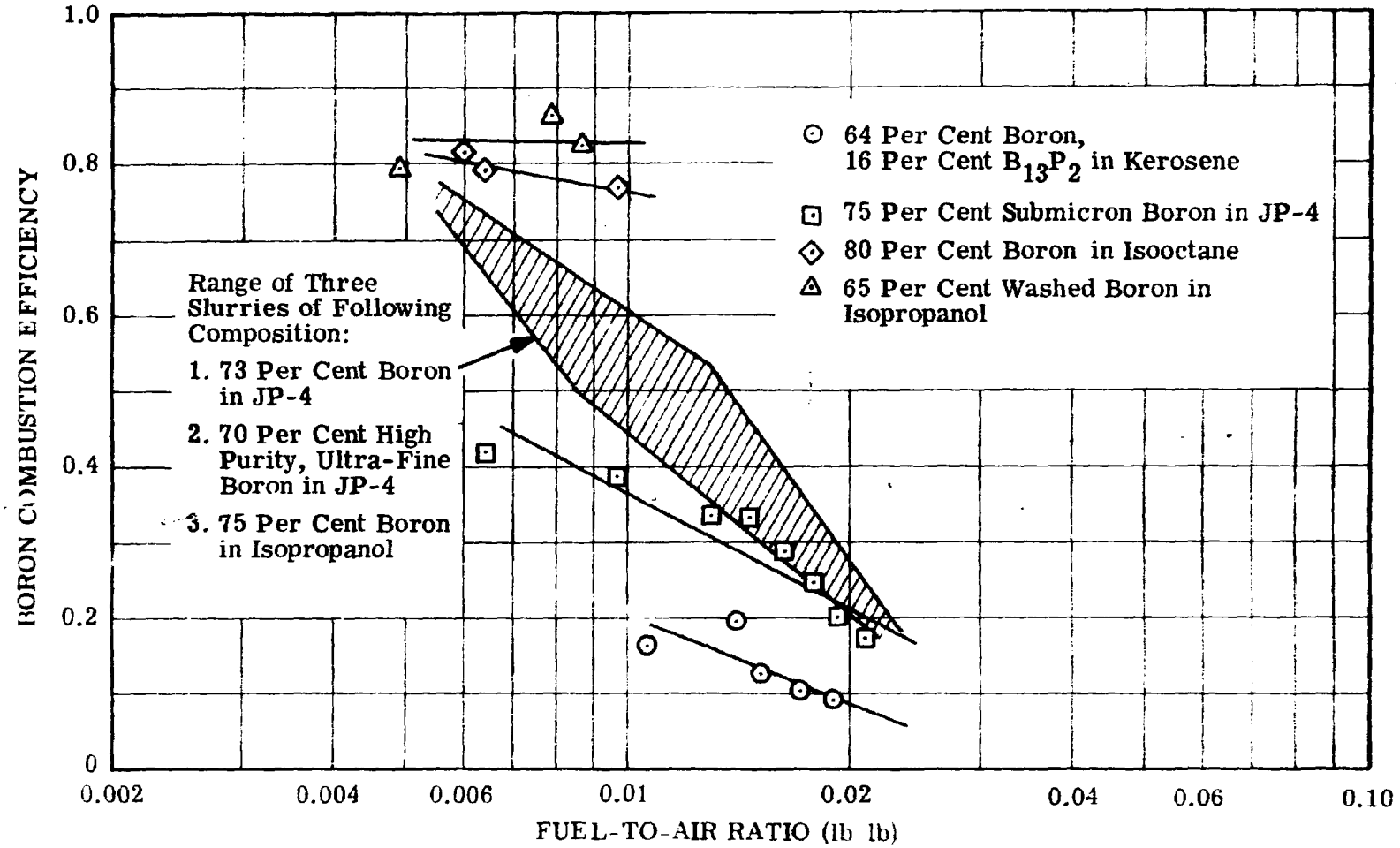

Figure 47. Composite Results of Combustion Efficiency Data from 3.5-inch Micro-Ramjet Test Series with Particle Mill Injection. Inlet Conditions - Mach 2.5 at Sea Level.

TABLE XXV

RELATIVE RANKING OF SEVEN BORON SLURRIES ON THE BASIS OF COMBUSTION PERFORMANCE IN THE 3.5-INCH MICRO-RAMJET TEST ENGINE (INLET CONDITIONS MACH 2.5 AT SEA LEVEL)

Slurry	Test No.	Combustion Efficiency Ranking	Volumetric Heat Release Ranking (at f/a = 0.01)	Possible Reasons for Deviations from "Standard" Performance
65% Washed Boron in Isopropanol	7	1	2	(1) Small particle size resulting from atomization; (2) possible enhancement due to surface cleanliness
80% Ball-Milled	15	2	1	(1) Very volatile carrier; (2) Extreme dilatancy may have enhanced atomization efficiency
73% Ball-Milled Boron in JP-4	1,12,13	3*	4	---
75% Ball-Milled Boron in Isopropanol	3,14	3*	3	---
70% High Purity, Ultra-Fine Boron (Ball-Milled) in JP-4	4	3*	5	---
75% Submicron Boron (Ball-Milled) in JP-4	6	6	6	(1) Large, tightly held agglomerates were formed in ball-milling process and were observed in exhaust samples.
64% Ball-Milled Boron, 16% $B_{13}P_2$ in C_{12} Kerosene	2	7	7	(1) Non-volatile carrier; (2) $B_{13}P_2$ particles were relatively large (up to 100μ)

* Indicates "Standard" Performance

4.4.3.2 Comparison with Marquardt Results

The results obtained with the 3.5-inch micro-ramjet did not agree quantitatively with the data obtained by The Marquardt Corporation in the 6.3-inch ramjet test engine, as shown on Figures 41, 42, and 43. The most reasonable course of this difference is the much smaller size (both length and diameter) of the micro-ramjet, which produces a significant reduction in residence time in the combustor.

When this difference in residence time is taken into account, it is believed that the qualitative agreement of the micro-ramjet data with the Marquardt data is excellent. For both test engines, combustion efficiency peaks at about 0.01 f/a and decreases steadily as fuel-to-air ratio is increased. The relative ranking of the fuels based on combustion efficiency is also the same for both engines, as indicated by Figures 41, 42, and 43. In addition, very similar burnthroughs in the burner can skirt were obtained with the more active slurries with both engines (burnthroughs are described later in this section). This qualitative agreement assures that the results of future testing in the micro-ramjet can be extrapolated to performance in another particle-mill-equipped engine on a relative basis; in other words, fuels which are ranked in a certain order in the micro-ramjet can be expected to perform according to this ranking in a larger ramjet engine.

4.4.3.3 Methods of Performance Measurement

As indicated by the data on Figures 41 through 46, combustion performance based on exhaust sampling agrees very well with thrust measurement when the combustion efficiency of the carrier is assumed equal to that of the boron. These two methods of measurement appear to provide adequate determination of combustion performance when used together. Good agreement was also obtained between combustion efficiencies based on thrust and on total pressure measurements; however, the presence of the pressure rake appeared to result in particle size sorting at the exhaust, rendering the exhaust sampling method, at a single position, unacceptable for use in combination with the total pressure rake. A comparison of the chemical data with and without the pressure rake is presented on Table XXVI.

TABLE XXVI

COMPARISON OF RESULTS OF EXHAUST SAMPLE ANALYSIS WITH AND WITHOUT THE TOTAL PRESSURE RAKE. COMBUSTION IN THE 35-INCH MICRO-RAMJET TEST ENGINE AT INLET CONDITIONS OF MACH 2.5, SEA LEVEL, COLD DAY.

Test No. 1, without the pressure rake.
Tests No. 12 and 13, with the pressure rake. The fuel was 73% boron in JP-4.

Fuel to Air Ratio lb/lb	Average Combustion Efficiency from thrust	Combustion Efficiency from Exhaust Analysis		
		Test 1	Test 12	Test 13
0.006	0.62*	0.75	0.79	0.65
0.008	0.54	0.49	0.61	0.69
0.012	0.44	0.43	0.54	0.55
0.014	0.43	0.41	0.47	0.43
0.017	0.40	0.34	0.42	0.41
0.020	0.36	0.30	0.41	0.30

*Probably a low value because of gas in the fuel, producing a reduction in density.

Although comparison of combustion efficiencies between thrust and total pressure resulted in good agreement (see Tables XXII, XXIII, and XXIV), somewhat less agreement was achieved between the measured values of P_{T_5} and those calculated from thrust measurement, as shown on Table XXVII. However, the bare-duct calibration test (Test 11) for the pressure rake produced a very reasonable total pressure distribution as shown on Figure 48.

Based on the experience obtained in using the three methods of evaluating slurry combustion performance, it is believed that the most efficient and beneficial technique for use with the micro-ramjet engine is the combination of thrust measurement and exhaust sampling.

4.4.3.4 Burnthroughs and Slurry Deposition

In Test 1 (for 73 per cent boron in JP-4, the burner can was destroyed by the combustion process, as shown on Figure 49. The type of burnthrough and even the pattern of the metal loss are very similar to those experienced by Marquardt with similar burner cans and slurry formulations[8]. The burnthrough in Test 1 appeared to occur mainly at a fuel-to-air ratio of 0.023, since at this condition molten metal from the can lodged on the downstream duct wall and caused a burnthrough at that location.

Motion pictures were taken of the burner can through the quartz window during Tests 3, 4 and 7 in which burnthroughs similar to that of Test 1 also were experienced. These movies show that the burnthroughs in the burner can occur at a fuel-to-air ratio of about 0.01 for each of these tests. A slight burnthrough also was experienced in Test 6 at an f/a of about 0.01. Although there appears to be a correlation between the extent of burnthrough and slurry burning characteristics, no complete interpretation is possible. These results do indicate that in tests involving cold flow prior to ignition that burner can is probably protected by a buildup of cold-flowing slurry, which coats the burner-can section with a material (dried slurry) of fairly low thermal conductivity. However, this probably is not desirable, generally, because this procedure would result in changing combustion conditions at the wall, loss of slurry prior to ignition, and increased burner drag.

TABLE XXVII

COMPARISON OF MEASURED VALUES OF P_{t_5} AVERAGED FROM PRESSURE RAKE DATA WITH VALUES OF P_{t_5} CALCULATED FROM THRUST MEASUREMENTS IN BORON SLURRY COMBUSTION TESTS 13, 14, AND 15 PERFORMED IN THE 3.5-INCH MICRO-RAMJET TEST ENGINE (INLET CONDITIONS - MACH 2.5, SEA LEVEL, COLD DAY)

TEST NO. 13 SLURRY OF 73% BORON IN JP-4		TEST NO. 14 SLURRY OF 75% BORON IN ISOPROPANOL		TEST NO. 15 SLURRY OF 80% BORON IN ISOOCTANE	
P_{t_5} FROM RAKE MEASUREMENT psia	P_{t_5} FROM THRUST psia	P_{t_5} FROM RAKE MEASUREMENT psia	P_{t_5} FROM THRUST psia	P_{t_5} FROM RAKE MEASUREMENT psia	P_{t_5} FROM THRUST psia
103.6	108	96.4	99	99.2	103
108.2	113	105.8	107	104.7	107
110.3	111	110.7	112	104.8	111
112.4	120	112.2	113	110.2	115
115.8	122	114.4	113	113.2	120
117.8	124	115.0	113	113.5	121
Average Deviation 5.0 psia		Average Deviation 1.5 psia		Average Deviation 5.2 psia	

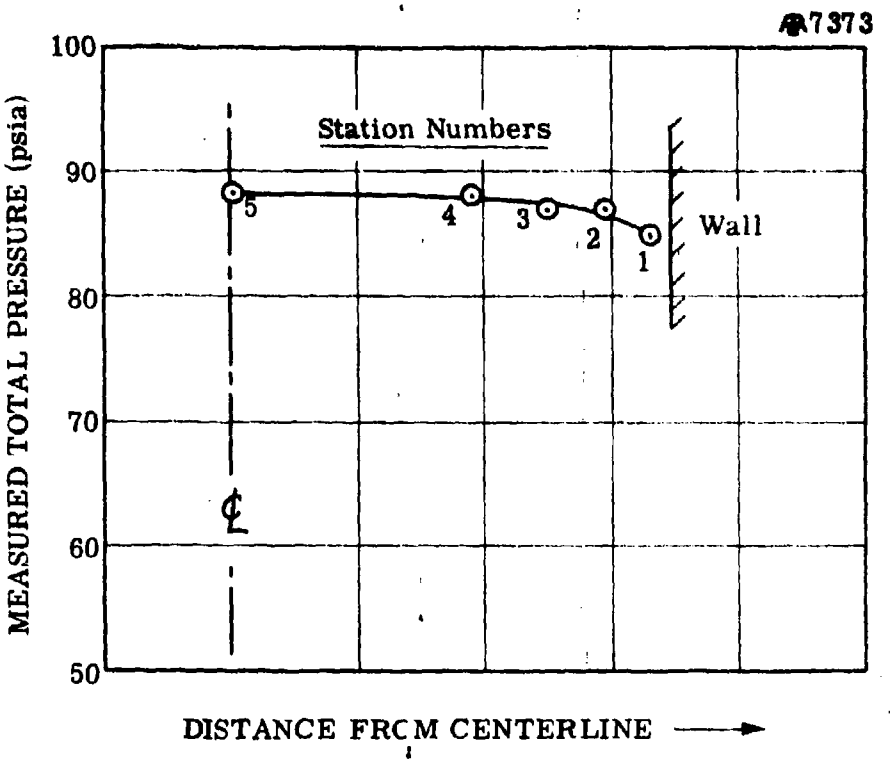

Figure 48. Total Pressure Distribution Across the Micro-Ramjet at the Nozzle Entrance as Determined by the Five-Point Total Pressure Rake (Test 11 - Bare-Duct Calibration).

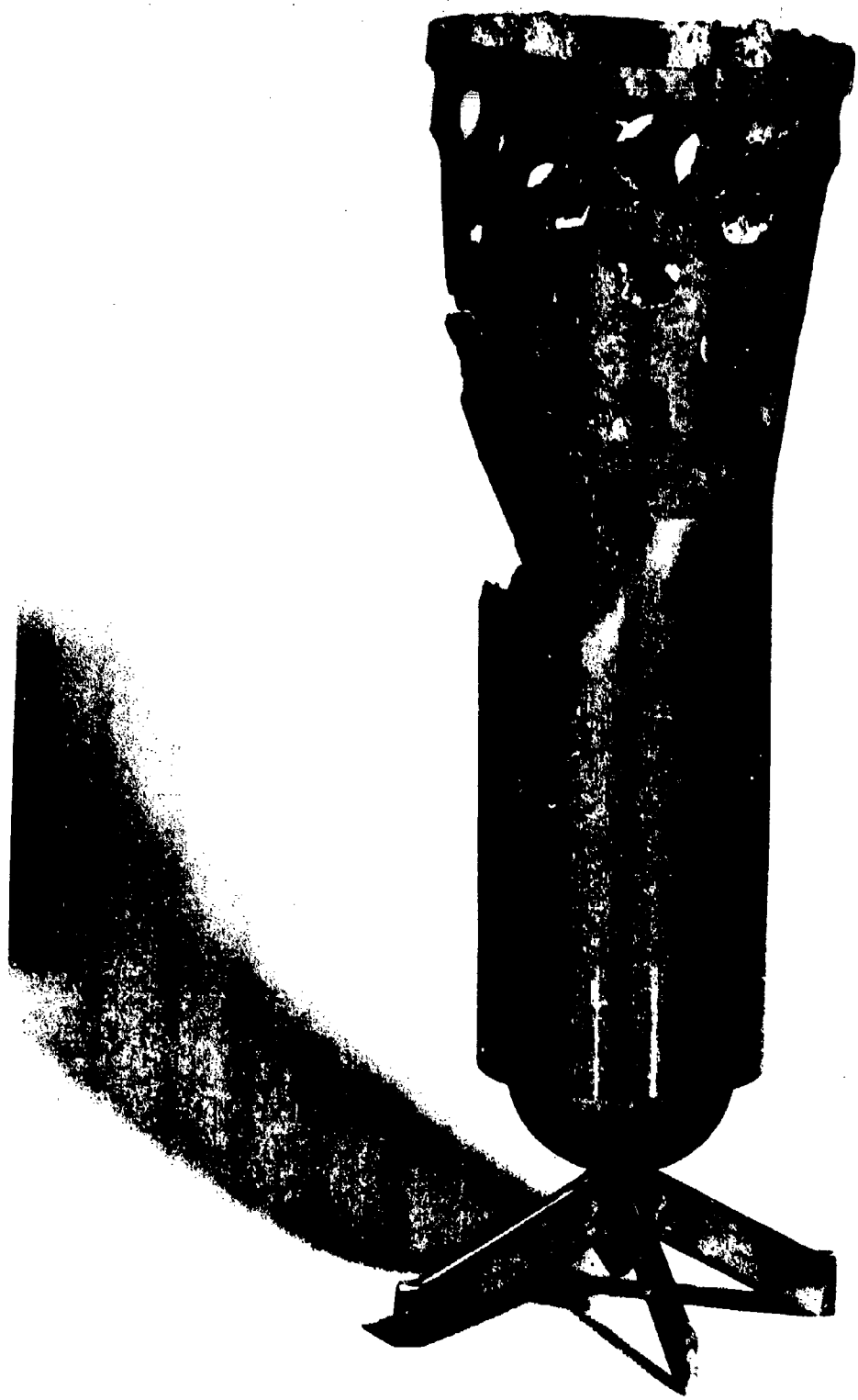

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Figure 49. Photograph of Micro-Ramjet Burner Can after Test No. 1. (Slurry of 73 Per Cent Boron in JP-4; Inlet Conditions Mach 2.5 at Sea Level; Fuel-to-Air Ratios 0.005 to 0.023).

A buildup of dried slurry on the burner can was observed with all the slurries, with the boron-$B_{13}P_2$ slurry in kerosene (Test 2) and the isooctane-based slurry (Test 15) producing slightly more buildup (and no burner can burnthroughs) than the other slurries; the slurry containing washed boron in isopropanol (Test 7) produced the least buildup. A photograph showing the slurry buildup which occurred during Test No. 2 (slurry of boron and $B_{13}P_2$ in kerosene) is presented as Figure 50. A comparison of Figures 49 and 50 indicates the similarity of buildup for the two cases (Tests 1 and 2). The buildup of fuel on the burner can during the tests corresponded to an increase in burner drag of from 21-23 psi at the beginning to 28-29 psi at the end of each run (except Test 6, which showed an unusually high drag of about 40 psi at the end of the test).

4.4.3.5 Interpretation of Thrust Trace Trends

The thrust traces for all fuels which burned well were strikingly similar; the total thrust leveled off to a constant value for values of f/a greater than 0.01 for all three fuels. In fact, for some fuels the thrust level was actually reduced by increased f/a in the range of 0.02. This is believed to be a strong indication that the stoichiometry of the mixture emerging from the particle mill has a very significant effect on the combustion process. At and below approximately stoichiometric conditions at the injector discharge location ($f/a \approx 0.01$) the combustion efficiency was good, but at fuel-rich conditions ($f/a > 0.01$) the combustion efficiency fell off rapidly. Perhaps this can be interpreted roughly as meaning that the air through the particle mill is that used mainly for combustion; and therefore, only a certain amount of fuel will burn regardless of the value of overall engine f/a. Of course, some combustion occurs downstream from the inlet holes in the skirt of the can, and this would provide some deviation from the effect hypothesized in the preceding sentence.

Plots of boron oxidation rate versus fuel-to-air ratio, such as the typical one, for Test 1, on Figure 51, indicate that the amount of boron burned per second (the boron oxidation rate) tends to approach a constant

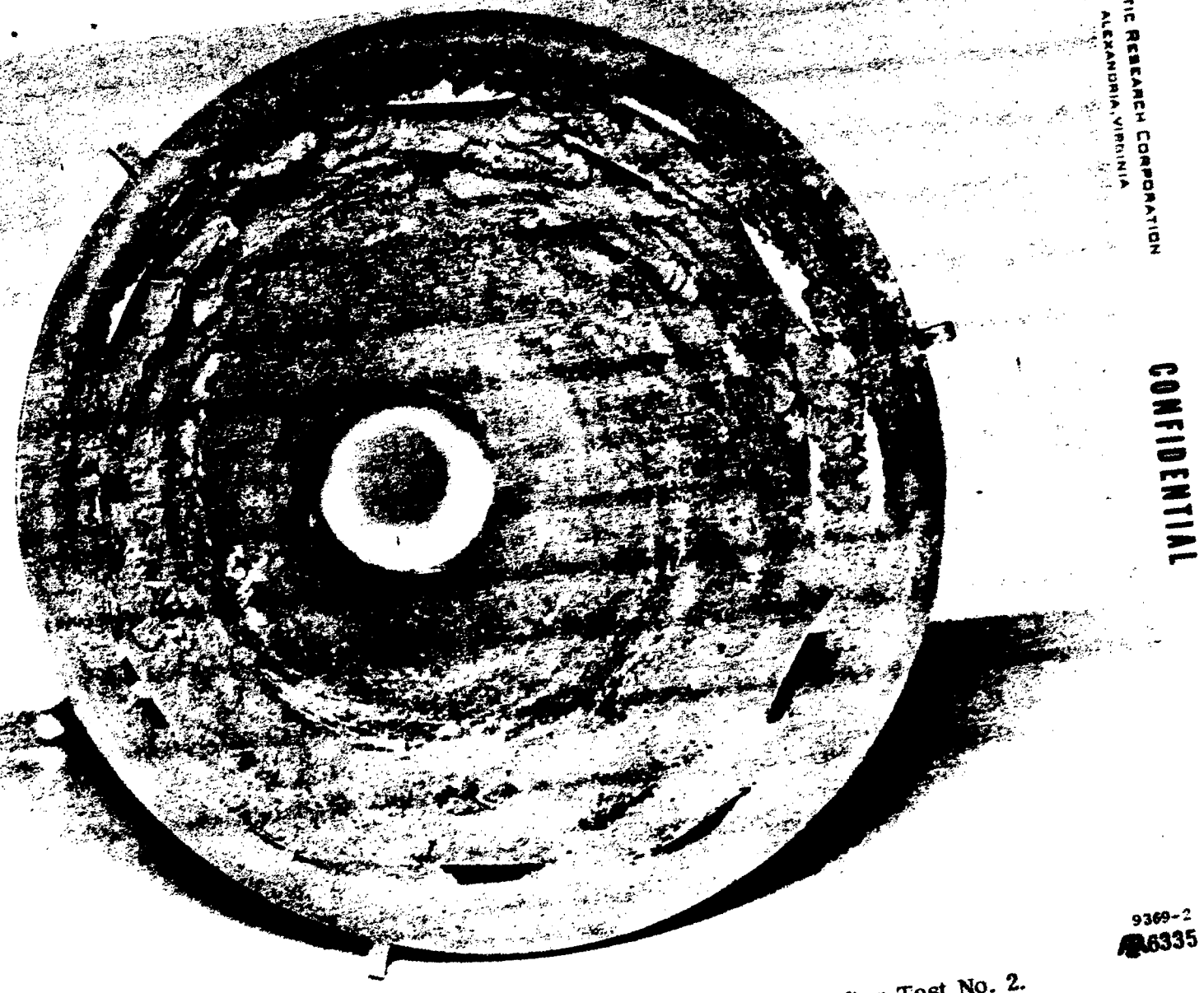

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Figure 50. Photograph of Interior of Micro-Ramjet Burner Can after Test No. 2. (Slurry of 64 Per Cent Boron, 16 Per Cent $B_{13}P_2$ in SO_2 - Extracted Paraffine Kerosene; Inlet Conditions Mach 2.5 at Sea Level; Fuel-to-Air Ratios 0.005 to 0.023).

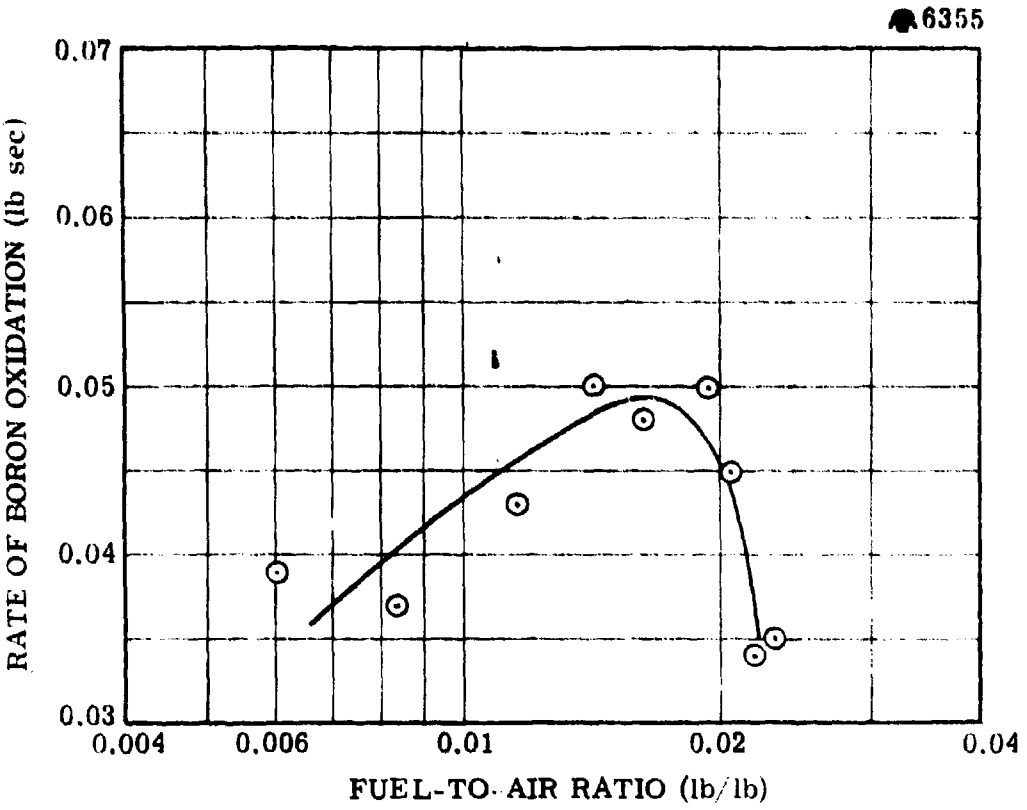

Figure 51. Plot of Total Boron Oxidation Rate Versus Fuel-to-Air Ratio for Combustion of a Slurry of 73 Per Cent Boron in JP-4 in the 3.5-inch Micro-Ramjet Test Engine with Particle Mill Injection (Inlet Conditions - Mach 2.5 at Sea Level).

value or decrease as the f/a is increased. This result is completely consistent with the hypothesis of the preceding paragraph; that is, that only a constant portion of the air (that which passes through the particle mill) is available for boron combustion. It should be noted here that the procedure followed in the tests reported herein consisted of incrementally increasing the slurry fuel flow rate, while maintaining a constant air flow rate, and data were recorded continuously.

4.4.3.6 Limitations of Data Collection and Analysis

Determination of boron combustion efficiency by chemical analysis of exhaust samples appears to produce a reliable qualitative comparison of slurry performance. In fact, the chemical data appear to be more consistent throughout the runs than the efficiencies calculated from thrust measurements.

The "sorting" of solid particles, corresponding to a nonuniform concentration distribution across the exit plane of the nozzle, which was evident in the 1964 work[2] did not appear to occur in these tests, except for those in which the pressure rake was positioned just upstream of the sampler head. The explanation for the increased reliability of the isokinetic sampler for determining combustion efficiency in the present runs is the five-fold increase in mass flow rate through the engine in the low altitude runs as compared with the high altitude conditions used in the 1964 tests. Because of the higher mass flow, mixing in the burner can has been increased, probably sufficiently to permit a uniform concentration distribution at the exit. The increased length of the engine duct in this series of tests may also have aided in increasing the accuracy of the exhaust sampling data.

Therefore, the major limitations of the chemical sampling method of determining slurry performance are the accuracy of the analytical method and the fact that the combustion efficiency of the carrier was not determined. It is believed that the accuracy of the analysis is within one or two per cent. Also, by comparing the thrust results with the sampling results, an estimate of carrier combustion efficiency may be obtained. In the case of

the tests conducted thus far, the combustion efficiencies of the various carriers appear to be in the range of 40 per cent (at low boron efficiencies) to 70 per cent (at high boron efficiencies). These efficiencies could probably be increased by an increase in residence time in the burner.

The calculation of combustion efficiency (η_B) on the computer (see Appendix II) involves convergence of the nozzle exit velocity with the sound speed at that station, for which the values of η_B are improved until the calculated thrust matches the measured thrust. This procedure requires that the combustion efficiency of the carrier be a known function, either a constant or a function only of the combustion efficiency of the boron. In the case of Test 2 (boron and $B_{13}P_2$ in SO_2-extracted paraffinic kerosene), it was found that the assumption of complete carrier combustion in all cases was far from valid, since the calculated combustion efficiency of the boron resulting from this assumption would have to be negative for convergence of the exit velocity and sound speed (and, also, calculated and measured thrust) in the program. However, the assumption that the carrier combustion efficiency was equal to that of the boron resulted in overall combustion efficiency data which were internally consistent in all cases. Close inspection of the data reveals the possibility that the combustion efficiency of the carrier might have been lower than that of the boron at the lower values of f/a and higher than that of the boron at the higher values of f/a. This would account for the slight difference in slopes of η_B versus f/a between the chemical data and the thrust data observed for most of the runs.

The computer program compared programmed values of burner drag with values determined by pressure measurements. The programmed values of burner drag produced consistent results for all tests except No. 6, for which burner drags as high as 40 psi were indicated by both the results of chemical sampling and pressure measurements on the engine. The values presented for Test 6 represent the data resulting from correction of the burner drag for this case. Although this test (Test No. 6) resulted in a fairly heavy deposition of unburned and burned slurry on the can walls, the deposition

was not quite as thick as in Tests 2 or 15 (see Figure 50) even though the pressure drop was much higher.

In several tests (notably Test 13) the initial data points (at the lowest values of f/a) from exhaust sampling and thrust measurement showed poor agreement. This difference is believed to be caused by the presence of air or other gas in the fuel. The value of f/a, which is calculated from the rpm of the ram, is in error on the low side when voids are present; therefore, the theoretical heat release calculated from the fuel flow rate is in error on the high side, causing the combustion efficiency based on thrust to be abnormally low. For later tests, the gas was eliminated by warming each slurry during the last stages of mixing and extruding it directly from the mixer into the ram.

4.4.3.7 Correlation with Ambient Pressure Combustor Results

The relative ranking of the slurry formulations tested in the micro-ramjet correlated well with the relative activity ranking obtained with the ambient pressure combustor, with the exception of one slurry. The iso-octane-based slurry (80 per cent solids - Test No. 15) performed poorly in the ambient pressure combustor, but exhibited high combustion efficiencies in the micro-ramjet tests. The comparison of the two rankings is presented on Table XXVIII.

Further work on non-dimensionalizing the ambient pressure data may provide a stronger basis of correlation between the two testing methods. For the present, however, it appears that the ambient pressure combustor can serve generally as an economical and reliable method of predicting differences in the combustion performance of slurry fuels containing the same carrier (assuming particle-mill atomization is used in the ramjet performance tests).

4.5 RESULTS OF FUEL EVALUATION STUDIES WITH THE DUAL-FLUID INJECTOR

The primary objective of these tests was to develop a method of evaluating slurry fuels which was not dependent upon the physical characteristics of the slurry, but with which factors such as the effects of primary

TABLE XXVIII

COMPARISON OF COMBUSTION PERFORMANCE RANKINGS OF VARIOUS SLURRY FUELS FROM MICRO-RAMJET DATA AND AMBIENT PRESSURE TEST RESULTS

Formulations	Micro-Ramjet Ranking	Ranking from Ambient Pressure Results
65% Washed Boron in Isopropanol	1	1
80% Ball-Milled Boron in Isooctane	2	7
73% Ball-Milled Boron in JP-4	3	3
73% Ball-Milled Boron in Isopropanol	4	2
70% High Purity, Ultra-Fine Boron (Ball-Milled) in JP-4	5	4
75% Submicron Boron (Ball-Milled) in JP-4	6	6*
64% Ball-Milled Boron, 16% $B_{13}P_2$ in SO_2-Extracted Paraffinic Kerosene	7	5

*Although this slurry could not be tested in the ambient pressure combustor because of the presence of large agglomerates, visual observations of its combustion place it as No. 6 in the rankings.

particle size and surface cleanliness could be evaluated. Secondary objectives included evaluation of various fuels using dual-fluid atomization, and observation of the combustion characteristics of a well-atomized cloud of boron dust. In order to accomplish these objectives the dual-fluid injector was designed to completely overpower the cohesive forces in the slurry, and the injector air pressure requirements were thus expected to be much higher than the 70 psia used in the ambient pressure combustor.

4.5.1 Check-Out and Calibration Tests

The primary goal of this series of three bare-duct tests with the dual-fluid injector was to establish the injector air pressure and gap spacing to be used. Slurry was atomized at injector air pressures from 100 psig to 500 psig. Based on visual observation of the fineness of the resulting dust and the symmetry of the cone angle, a minimum pressure of 200 psig was established for gap spacings from 0.001 to 0.005 inches. Water was also used for visual testing of cone angles in later tests of diffuser inserts for the test section. This type of testing was continued throughout the period during which the fluid injector was used. As will be seen, different burner-can configurations were used for many of these tests, and almost all major alterations in can geometry required water and/or slurry cold-flow testing for adjustment of the resulting flow patterns.

Other check-out tests with the dual fluid injector included the determination of the thrust derived from injector air flow (this was found to be negligible) in Test 39 and a combustion test with JP-4 (no boron) in Test 35. In the latter test the JP-4 was found to burn at about 55 per cent efficiency over the fuel-to-air ratio range covered. This test is discussed in detail later in the report.

4.5.2 Test Conditions

The inlet air conditions (Mach 2.5 at Sea Level, Cold Day) and duct dimensions used in these tests were the same as those used for the particle mill tests. Somewhat higher fuel-to-air ratios were achieved with

the dual-fluid injector than with the particle mill, probably because the slurry stream was protected from carrier loss until it had passed through the limiting resistance of the flow system (the possibility of dilatancy caused by propagation or carrier loss through the fuel supply line was eliminated in the dual-fluid injector).

In most of the combustion tests with the dual-fluid injector the injector pressure was set at 500 psig and the gap spacing was 0.005 inch. The temperature of the injector air was the ambient condition. The flow rate of injector air at these conditions was about 0.05 lb./sec., or less than one per cent of the total air supplied at test conditions.

4.5.3 Test Results

Test Nos. 16 through 22 are described separately in this section in order to indicate the different burner configurations used. All of these tests were performed with the 1965 "workhorse" formulation of 73 per cent ball-milled boron (commercial grade) in gelled JP-4. The dual-fluid injector was used to atomize the slurry in each test.

4.5.3.1 Test Number 16

The burner can design used in Test 16 is shown in Figure 52. The air distribution was designed to admit 50 per cent of the air to the burner can. The remainder of the air passed between the can and the duct wall, mixing with the remaining fuel, combustion products, etc., downstream of the can.

In Test 16, flame-holding occurred at the tip of the injector, causing a burn-through in this location. This resulted in loss of atomization air pressure and, consequently, poor atomization. Analysis of exhaust samples indicated a maximum boron combustion efficiency of about seven per cent.

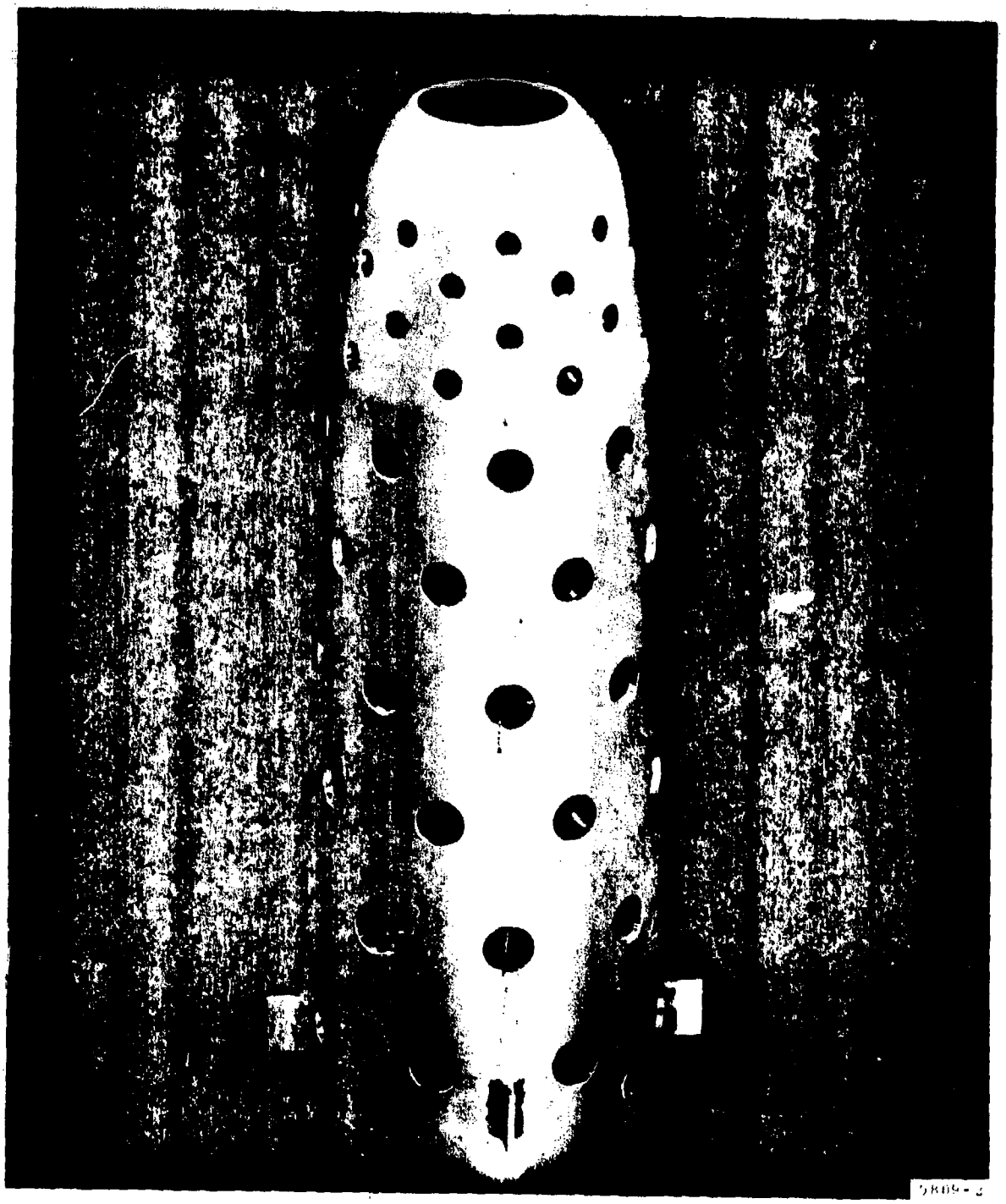

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Figure 52. Photograph of First Burner Can Designed for Use with the Dual-Fluid Slurry Injector in Micro-Ramjet Combustion Tests.

4.5.3.2 Test Number 17

Air inlet ports about the injector housing, shown in Figure 53, were provided for the burner can used in Test Number 16 in order to prevent further burnthroughs (to prevent recirculation in the region of the injector head). However, ignition was not achieved in Test Number 17.

4.5.3.3 Test Number 18

The same burner can configuration used in Test Number 17, and shown on Figure 53, was also used in Test Number 18. The hydrogen igniter was moved to a central location in the can to insure contact of the slurry stream with the hydrogen flame. Again, however, no ignition was achieved.

4.5.3.4 Discussion of Test Numbers 16, 17, 18

The poor results obtained from tests 16, 17, and 18 were clarified by the following analysis:

(1) Boron dust clouds cannot be piloted by combustion of vaporized carrier since the carrier itself does not readily ignite. This had also been illustrated by the particle mill tests in which a kerosene spray issuing from the particle mill could not be ignited in the micro-ramjet, but a dust cloud of atomized boron slurry could be ignited fairly easily.

(2) The velocity of the boron particles issuing from the dual-fluid atomizer was too high for ignition by the hydrogen (through heat transfer) to occur.

4.5.3.5 Test Number 19

In Test Number 19 a burner can was not used. The slurry was atomized into a diffuser tube (1.75-inch diameter by 5-inches long), shown on Figure 54, and the particles were allowed to slow down before contacting the main air stream. The igniter was placed at the exit of the diffuser tube. The diffuser tube ended at the viewing port, so

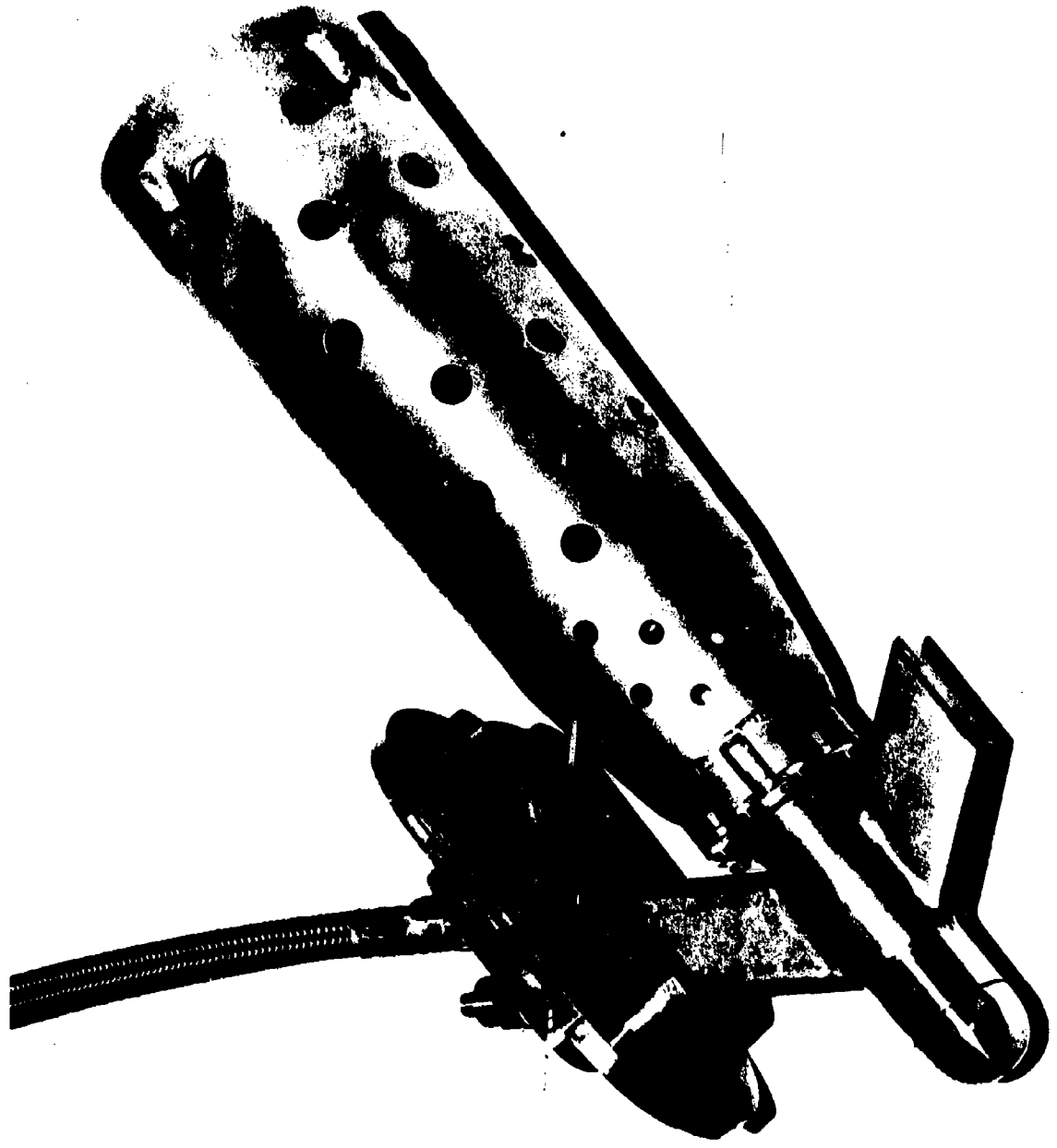

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Figure 53. Burner Can Used in Micro-Ramjet Tests 17 and 18.

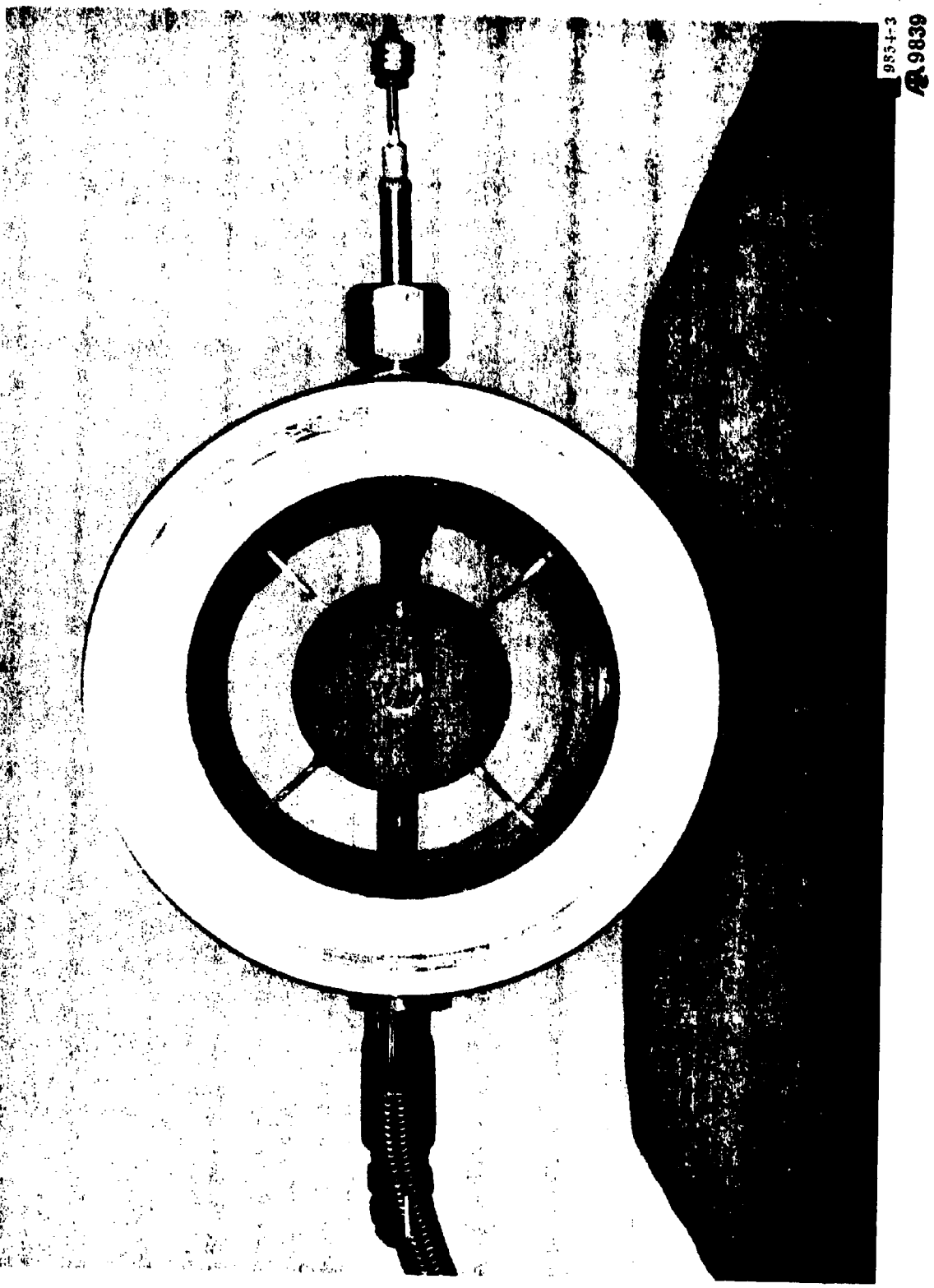

Figure 54. End View of Burner and Insert Used in Micro-Ramjet Test No. 19.

that any combustion could be photographed. No attempt at flame holding or mixing was made.

When the igniter was activated, immediate combustion occurred, and burning obviously occurred throughout the entire length of the duct, through the exit nozzle, and into the eductor system. The graphical representation of combustion efficiency (based on thrust) versus fuel-to-air ratio for this test is presented on Figure 55. Although the efficiency achieved was only about 25 per cent, the combustion efficiency was fairly constant throughout the range of fuel-to-air ratio covered. Combustion efficiencies obtained from analysis of exhaust samples were very erratic, indicating particle sorting due to the non-mixing situation near the center of the stream. Only slight deposition of unburned slurry occurred in this test, as shown in Figure 56.

4.5.3.6 Test Number 20

This test was essentially a repeat of Test Number 19, except that only a fraction of the injector air flow rate of Test 19 was used in Test 20 (in Test 19, the air gap widened due to faulty assembly of the injector, so that an unknown amount of air passed through the injector and down the diffuser tube), and a graphite insert was used to direct the flow in the diffuser tube. Combustion was obtained in Test 20, but it was erratic, and the resulting combustion efficiencies were somewhat lower than in Test 19. These results indicated that the admittance of a certain amount of primary air to the diffuser tube would be beneficial.

4.5.3.7 Test Number 21

The diffuser tube was pierced so that a small amount of primary air (roughly about 3 per cent) could enter the diffuser tube for mixture with the slurry dust cloud. A modification of the graphite

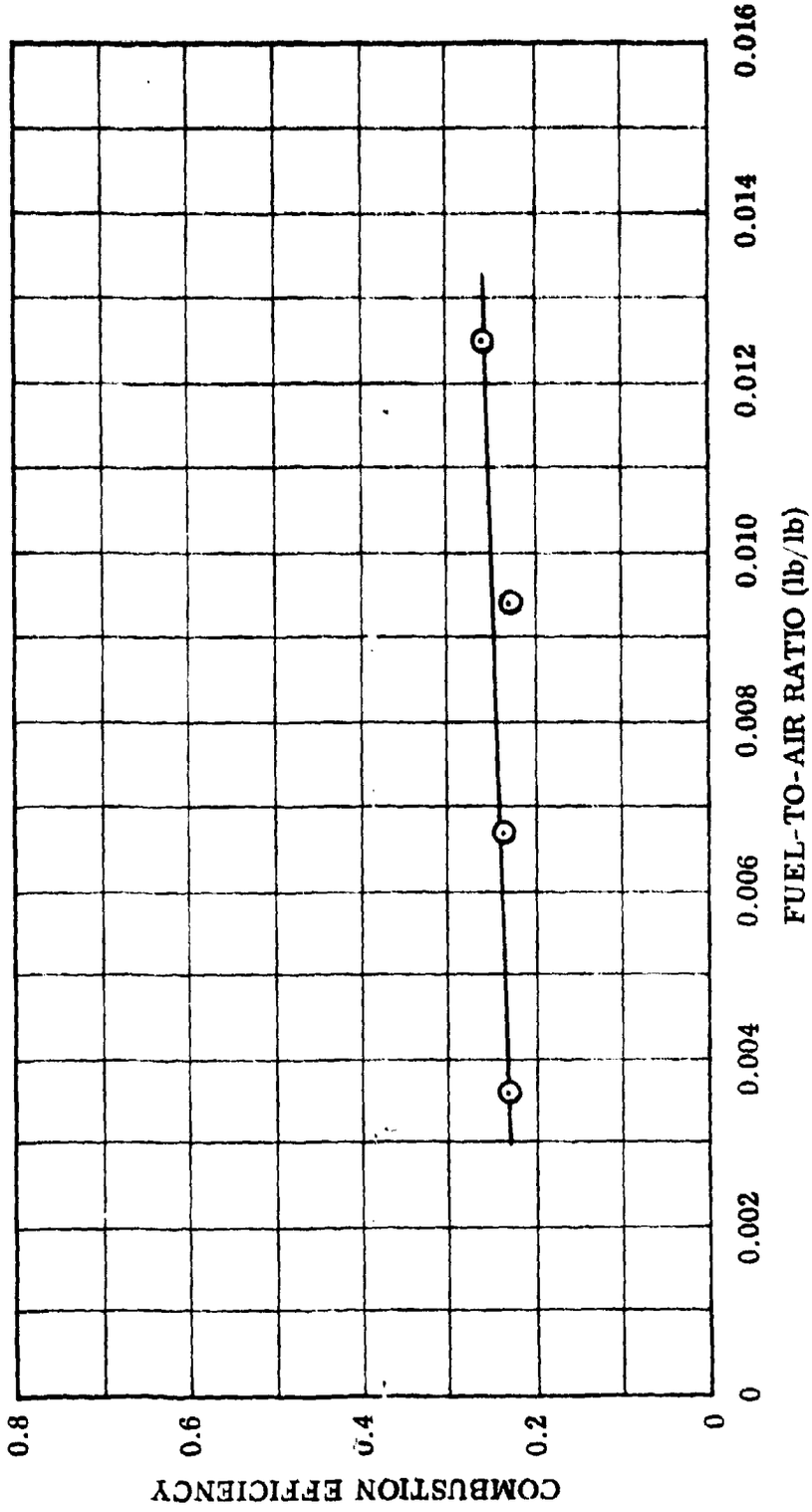

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Figure 55. Results of Micro-Ramjet Test No. 19 Determined by Thrust Measurement. Combustion of Slurry of 73 Per Cent Boron in JP-4 Under Inlet Air Conditions of Mach 2.5 at Sea Level, Cold Day. Dual-Fluid Injector was Used with No Flame-Holder or Stream Mixing Aids. Injector Air Pressure 500 psig.

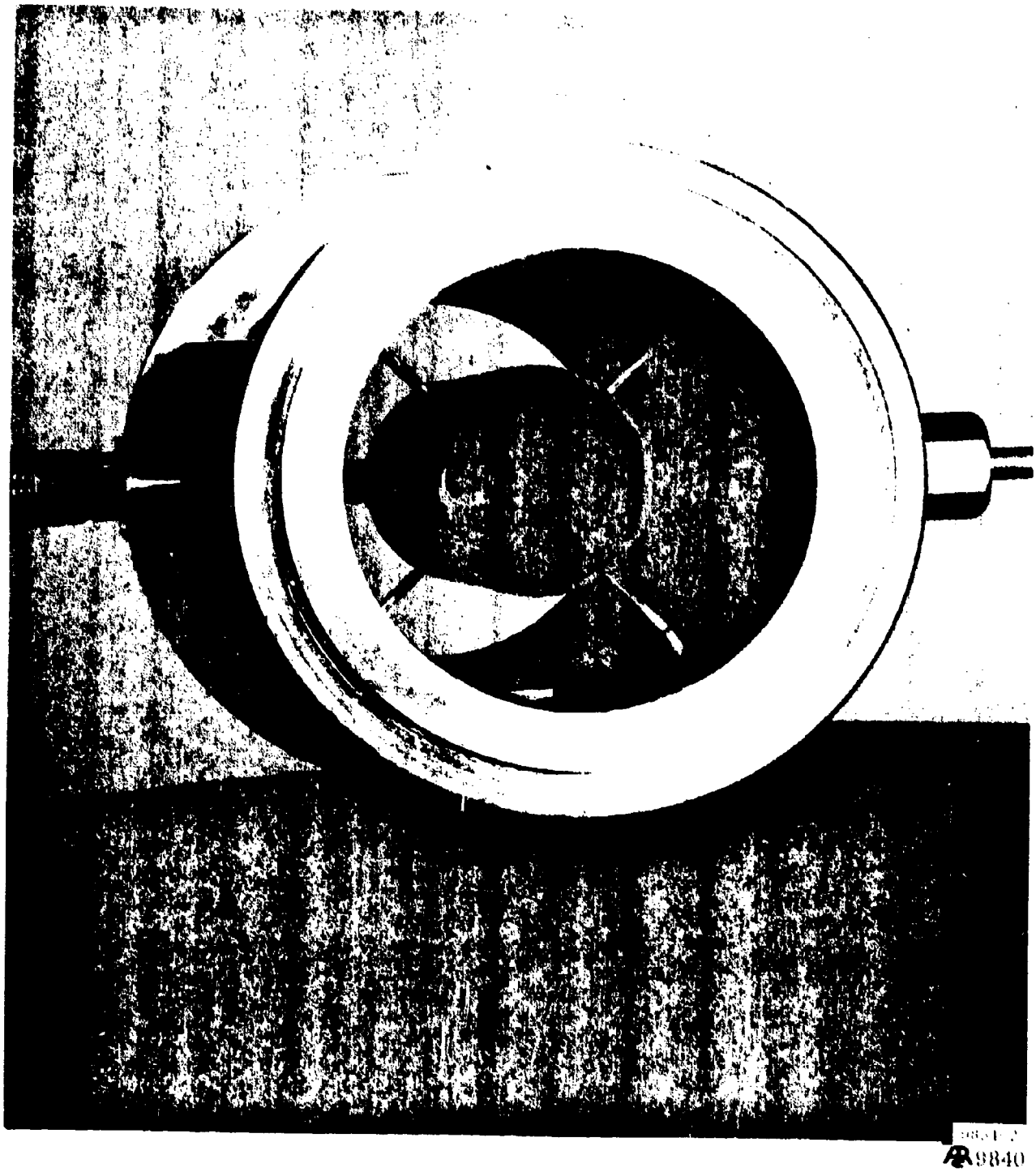

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Figure 56. Diffuser Tube After Micro-Ramjet Test No. 19.

insert used in Test 20 was also used in Test 21. The combustion efficiencies obtained from this test are compared on Figure 57 with average data from two particle mill tests with the same type of slurry. The plots for the two types of burners crossed, and the combustion efficiency for the test with the dual fluid injector (with no flame holding or mixing) was slightly higher than that for the particle mill tests at a fuel-to-air ratio of 0.02. The dual-fluid injector also allowed operation at an f/a of 0.03, which could not be achieved with the particle mill because of the higher pressure drop required to inject the slurry stream into the hot-gas environment of the particle mill.

A photograph of the diffuser tube after Test 21 is shown on Figure 58.

4.5.3.8 Discussion of Test Numbers 19, 20, 21

The results of these tests show that, under certain conditions, a dust of boron particles is extremely reactive. These tests also indicate that complicated hardware for flame holding may not be necessary (and, in fact, may be undesirable) for boron slurry combustion. The burning appeared to be pseudo-gaseous in nature, instead of the combustion of individual particles observed in many ambient pressure tests and micro-ramjet firings. Such pseudo-gaseous combustion can occur in dusts of small solid particles, but the particle size of boron necessary to permit such combustion is not known.

The injector-diffuser configuration used in Tests 19, 20 and 21 offer extremely low burner drags. The drag coefficients in these tests were typically about 0.8 to 0.9, as compared to burner drag coefficients of 5 to 7 for the particle mill-burner can combination. Increased mixing will, of course, increase these low values.

4.5.3.9 Results and Discussion of Test Number 22

In order to achieve substantial mixing of the fuel-rich stream and the main air stream, four right-angle scoops were placed

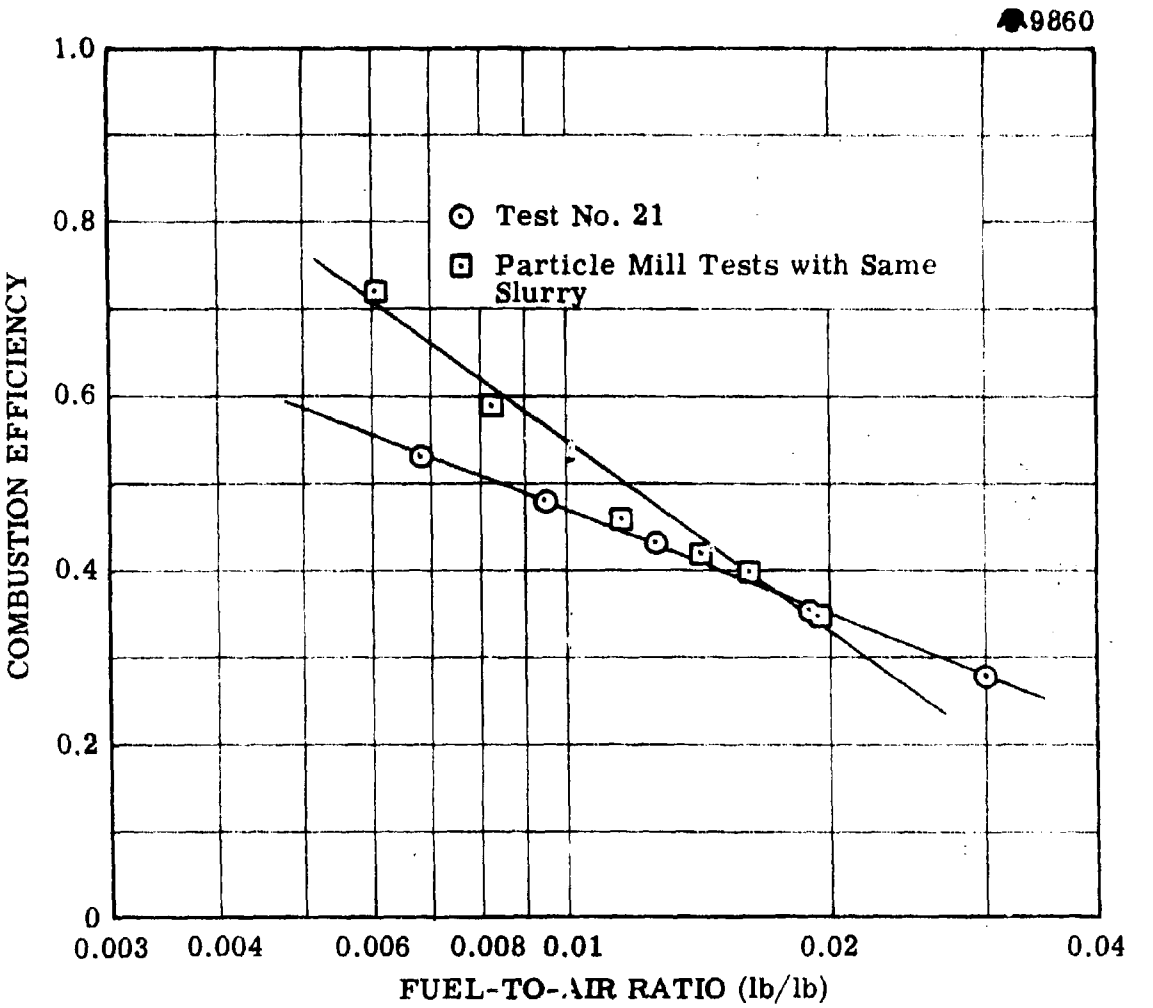

Figure 57. Results of Micro-Ramjet Test No. 21 Determined by Thrust Measurement. Combustion of Slurry of 73 Per Cent Boron in JP-4 Under Inlet Air Conditions of Mach 2.5 at Sea Level, Cold Day. Dual-Fluid Injector was Used with No Flame Holder or Stream Mixing Aids. Injector Air Flow Rate was 0.05 lb/sec, and Injector Air Pressure was 500 psig.

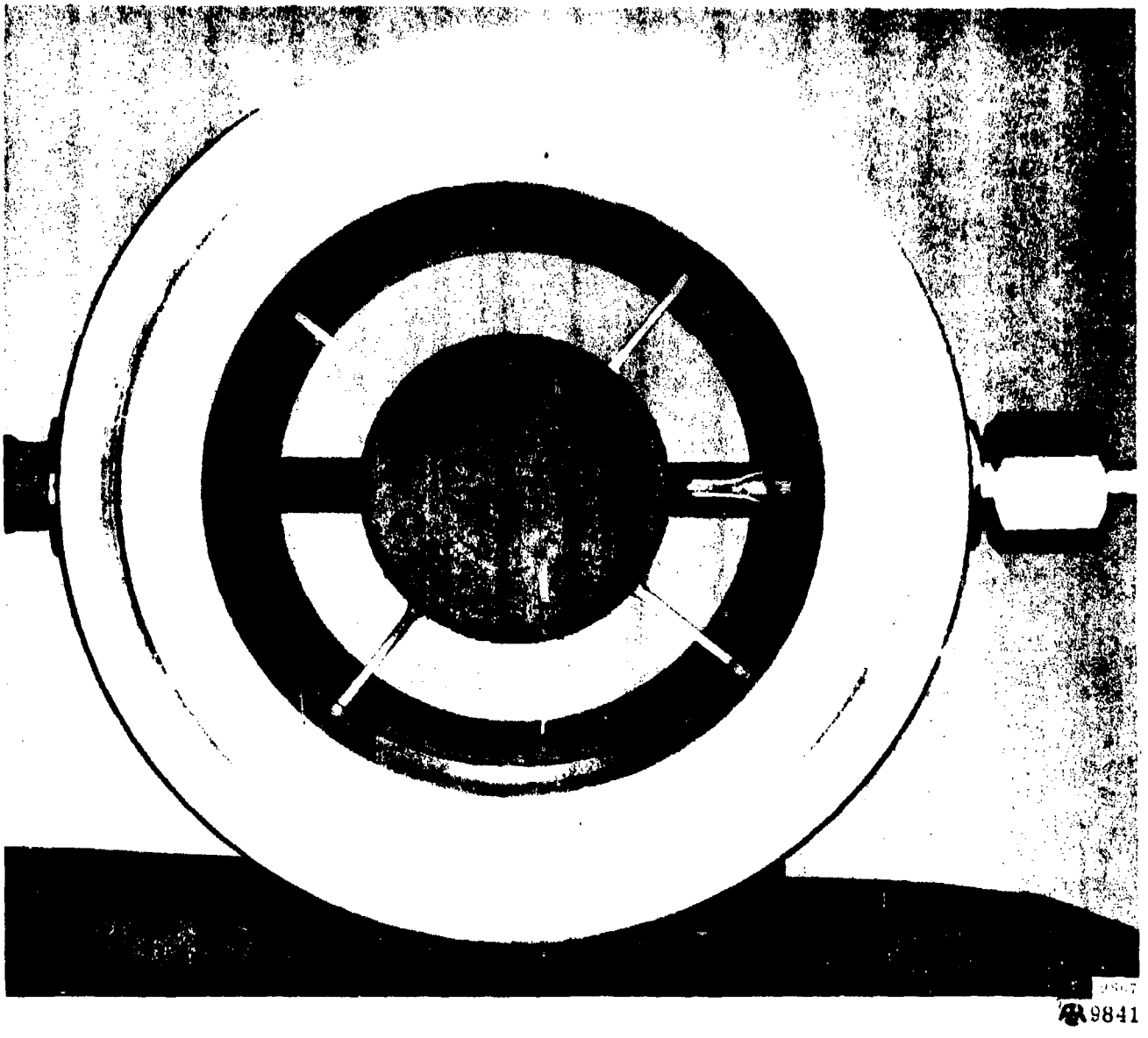

Figure 58. Photograph of Diffuser Tube After Test 21.

about the end of the diffuser tube. The purpose of these scoops, or air diverters, was to supply air to the center of the fuel-rich effluent from the diffuser, thus mixing the boron particles with the main air stream within a short distance. The scoops are shown on Figure 59, which was taken after the test.

Although fair combustion was achieved in Test 22, especially at the lower values of f/a, the combustion efficiencies appear to be lower than those of the preceding test with no attempt at mixing. (The data are presented on Figure 60) These results strongly indicate that the slurry flame was quenched by the sudden admixture with the primary air stream. This type of quenching, which has been discussed previously with regard to the particle mill-burner can configuration used with the micro-ramjet engine, appears to be a critical factor which has a very significant effect on the ability of a burner to attain good slurry combustion performance. Furthermore, the conditions producing good combustion and those resulting in quenching may be fairly similar. In this case, the particle size of the atomized slurry would be expected to become the critical parameter in obtaining complete combustion.

The quenching hypothesized as having occurred in Test 22 could not be expected to occur for the same mixing conditions for different types of slurries. This could partially explain the discrimination between fuels exhibited by the particle mill-Marquardt 8A burner can combination (in which mixing conditions are fixed) in previous testing.

4.5.3.10 Tests 23 through 29

A summary of Tests 23 through 29 is presented on Table XXIX. Photographs of the test sections used in these tests are presented in the figures noted in Table XXIX. Combustion efficiency data for tests

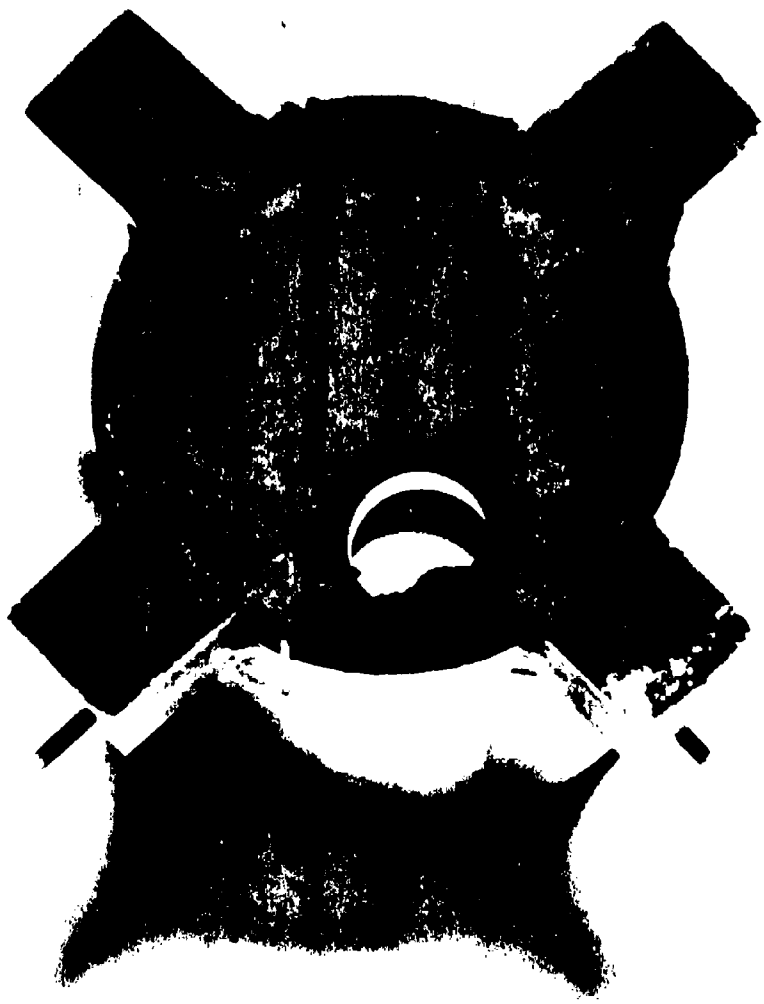

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Figure 59. Diffuser Tube for Boron Slurry Combustion After Micro-Ramjet Test No. 22.

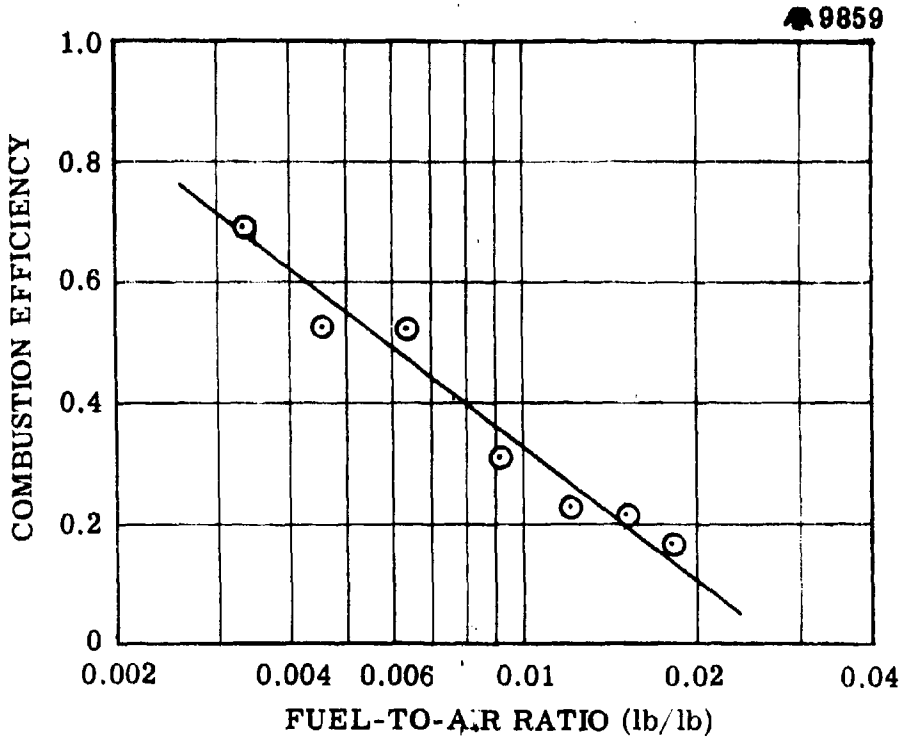

Figure 60. Plot of Combustion Efficiency Versus Fuel-to-Air Ratio for Boron Slurry Test No. 22 in the 3.5-inch Micro-Ramjet. Inlet Conditions were Mach 2.5, Sea Level, Cold Day. Fuel was 73 Per Cent Boron in JP-4 (1965 Workhorse). In this Test Efficient Mixing Occurred Downstream of the Diffuser Tube.

TABLE XXIX

SUMMARY OF 3.5-INCH MICRO-RAMJET COMBUSTION TESTS 23 THROUGH 29 WITH BORON SLURRIES. INLET CONDITIONS MACH 2.5 AT SEA LEVEL, COLD DAY FUEL INJECTION BY DUAL-FLUID ATOMIZER, INJECTOR AIR PRESSURE 500 PSIG.

Test No.	Fuel	Burner Configuration	Comments
23	73% ball-milled commercial boron in gelled JP-4	Vortex generator added around periphery of shrouded diffuser tube (Figure 61)	Combustion fair, but not sustained at higher f/a
24	Same as 23	Increased primary air through diffuser tube	No combustion
25	Same as 23	Shortened diffuser insert to provide better flame holding (Figure 62)	Fair combustion up to 0.025 f/a
26	70% ball-milled ultra-fine, high purity boron in ungelled JP-4	Same as 25	Good combustion up to 0.025 f/a
27	75% ball-milled submicron boron in ungelled JP-4	Same as 25	Fair combustion up to 0.030 f/a
28	80% ball-milled commercial boron in methyl-isobutyl ketone	Same as 25	No sustained ignition; fuel dilated at f/a of 0.01
29	80% ball-milled commercial boron in gelled JP-4	Diffuser ring added to shroud to slow down air in combustion region	No sustained ignition; could not hold atomization air pressure, fuel dilated

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Figure 61. Diffuser Tube Used in Micro-Ramjet Test No. 25.

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Figure 62. Diffuser Tube Used in Micro-Ramjet Tests No. 23 and 24.

23 and 25 are presented in Figure 63.

Combustion efficiency data for Tests 26 and 27 (with ultra-fine and submicron boron, respectively) are compared with the data from Test 21 for commercial-grade (~1μ diameter) boron on Figure 64. These results indicate that the ultra-fine, high purity boron slurry delivered a much higher combustion efficiency than the commercial boron slurry. The poor showing of the submicron boron was undoubtedly due to large, tightly-held agglomerates formed during ball-milling. These agglomerates were noted in the exhaust samples from both the particle mill test (Test 6) and the dual-fluid injection test (Test 27) with this slurry.

In Tests 28 and 29, rheological problems prevented the 80 per cent loaded slurries in methyl-isobutyl ketone and gelled isooctane, respectively, from being combusted. These problems were at least partially caused by the very cold ambient conditions at the time of testing.

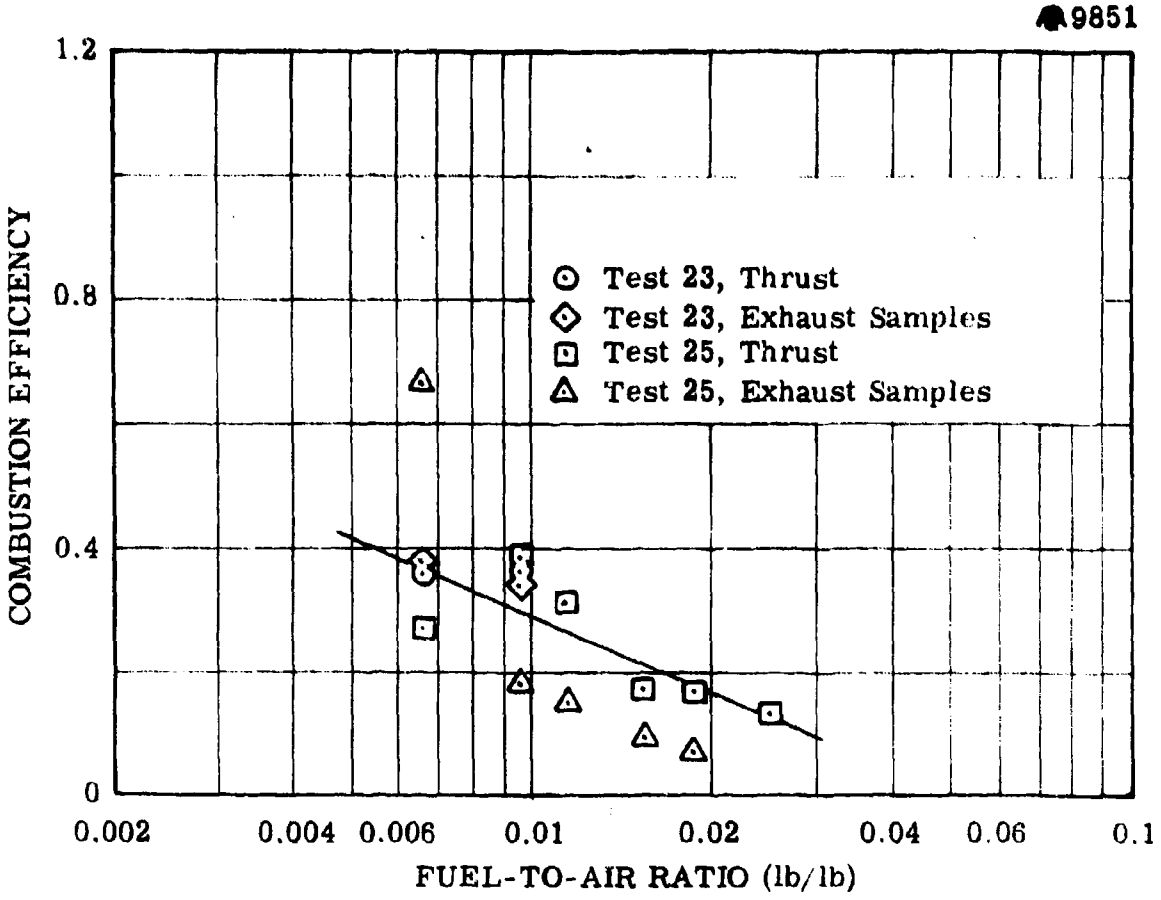

Figure 63. Results of Micro-Ramjet Tests 23 and 25 with Fuel of 73 Per Cent Boron in JP-4. Inlet Conditions Mach 2.5, Sea Level, Cold Day.

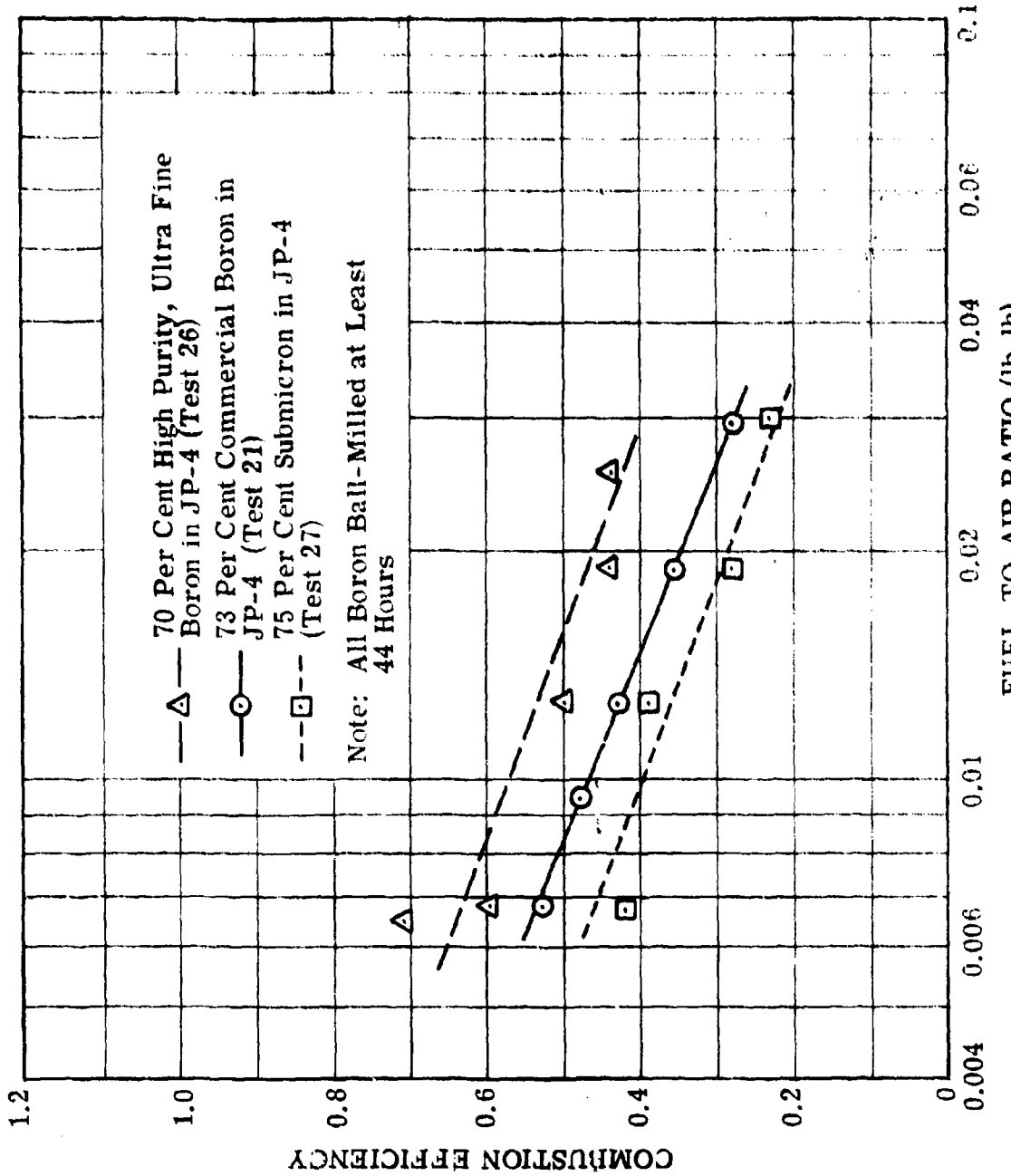

Figure 64. Comparison of Thrust-Based Combustion Test Results with Slurries of Three Types of Boron in 3.5-Inch Micro-Ramjet Test Engine Equipped with Dual-Fluid Atomization. Inlet Conditions - Mach 2.5, Sea Level, Cold Day. Injection Air Pressure 500 psig.

4.5.3.11 Tests 30 through 34

An injector air leak was found after Test 34, which rendered the results from Tests 30 through 34 invalid. The quality of the combustion in all of these tests (which utilized various slurries) was poor, indicating that the poor atomization resulting from air leak for this series strongly influenced the combustion properties.

In Test 34 a slurry of 80 per cent boron in isooctane was used, but very little flow was obtained before the rheological properties of the slurry caused rupture of the blow-out disc on the ram. As a result of this failure and the other problems encountered with slurries of 80 per cent solids (Tests 28 and 29), it was decided that no more slurries at solids loadings above 75 per cent would be tested under this program.

4.5.3.12 Test No. 35

The fuel used in Test No. 35 was JP-4 without boron or gellant. The diffuser used, shown on Figures 65 and 66, included a diffuser ring about the shroud to reduce the amount of air entering the combustion process at the end of the primary diffuser. The insert of the primary diffuser was also shorter than those used previously, so that initial flame stabilization could occur upstream of the primary diffuser exit.

As shown by Figure 67, the performance of the neat JP-4 (in terms of combustion efficiency) over the range of f/a was similar to that of the high purity, ultra-fine boron slurry (see Figure 64), except that the combustion efficiency of the neat JP-4 increased somewhat as f/a increased whereas the slurry performance was reduced as f/a increased. These results indicate that, for the dual-fluid injector as well as the particle mill injector configurations, the slurry carrier burns with about the same combustion efficiency as the boron does.

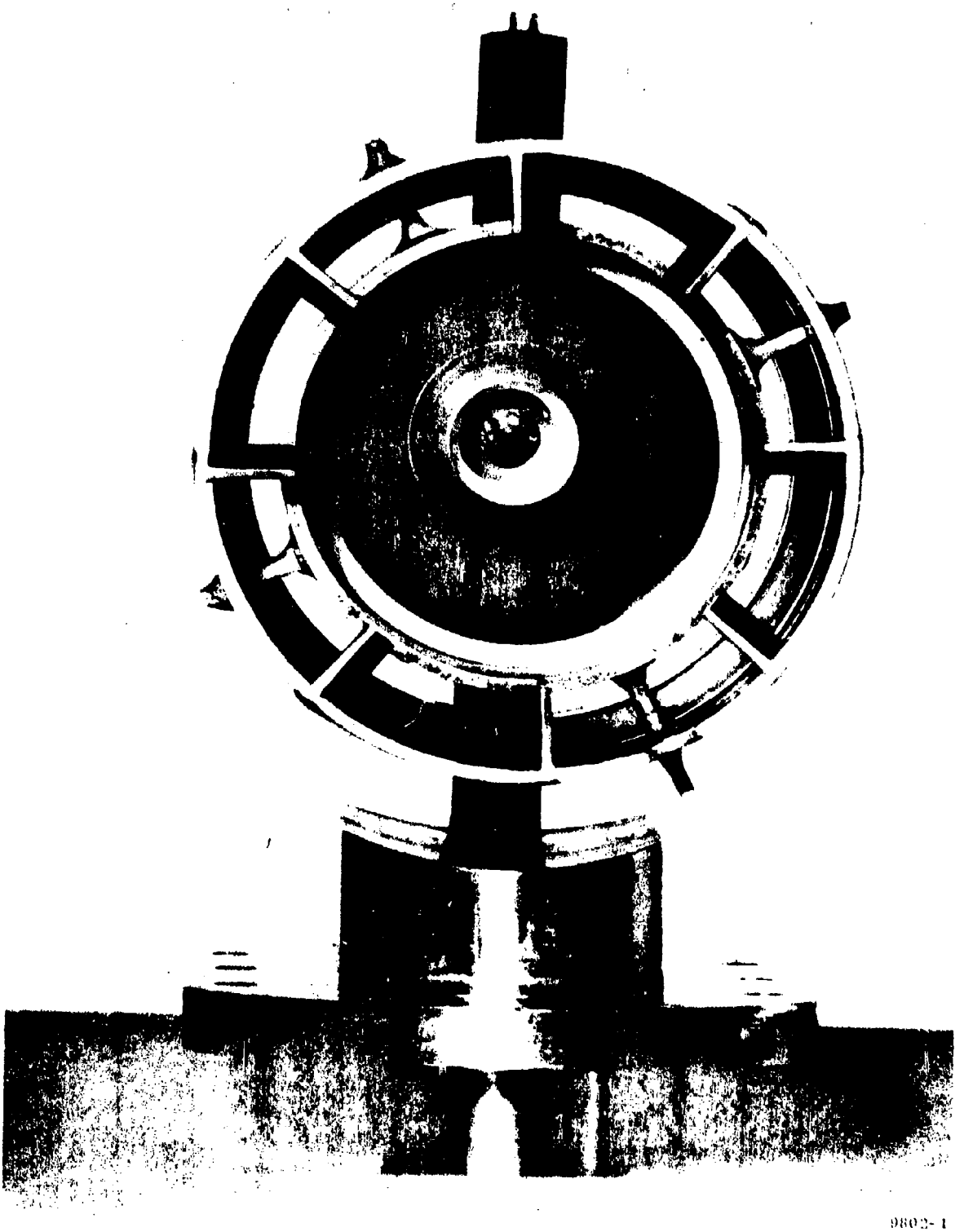

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Figure 65. Rear View of Diffuser Tube Used in Tests 35 Through 40.

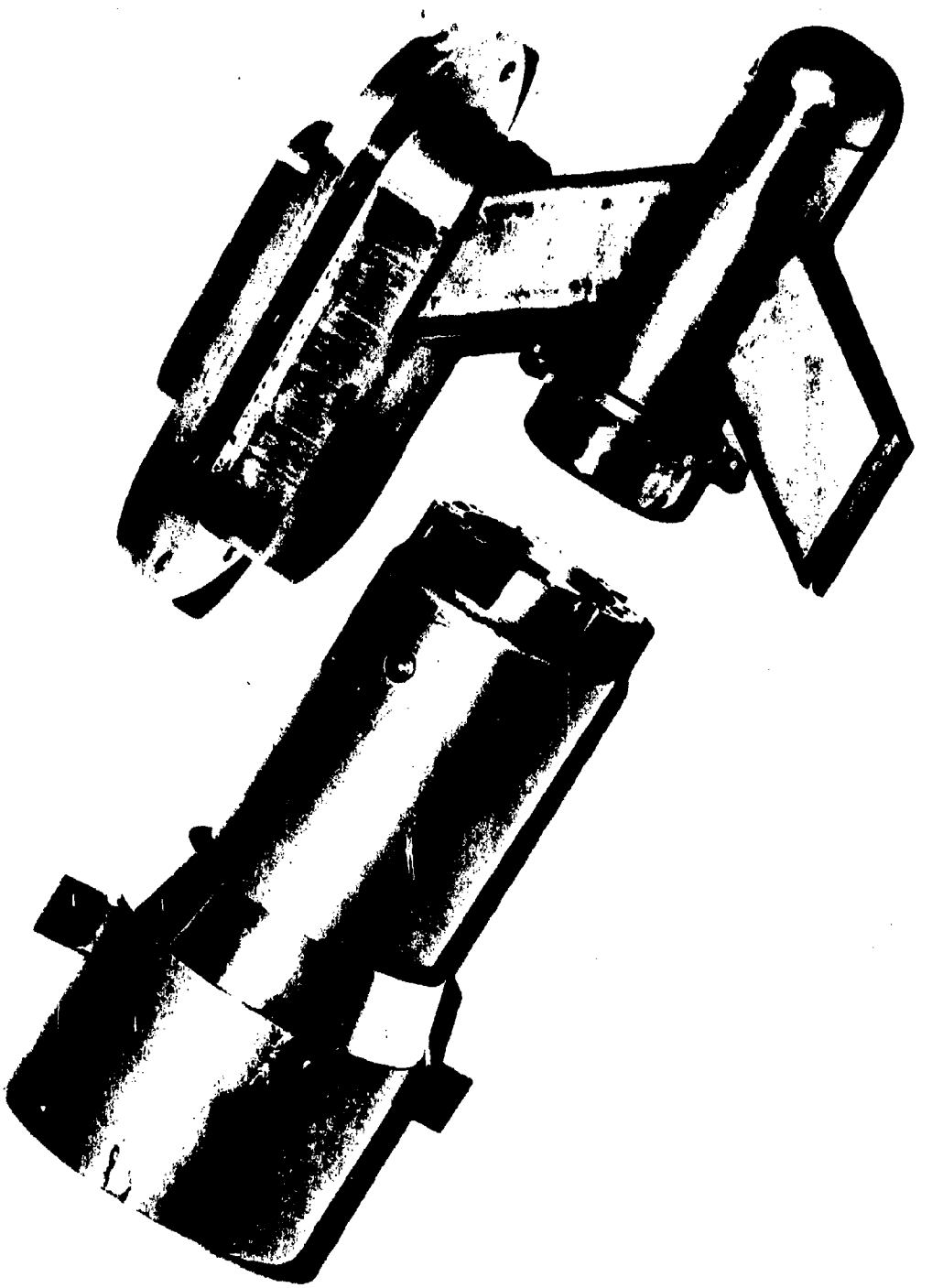

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Figure 66. Diffuser and Dual-Fluid Injector Used in Tests 35 Through 40.

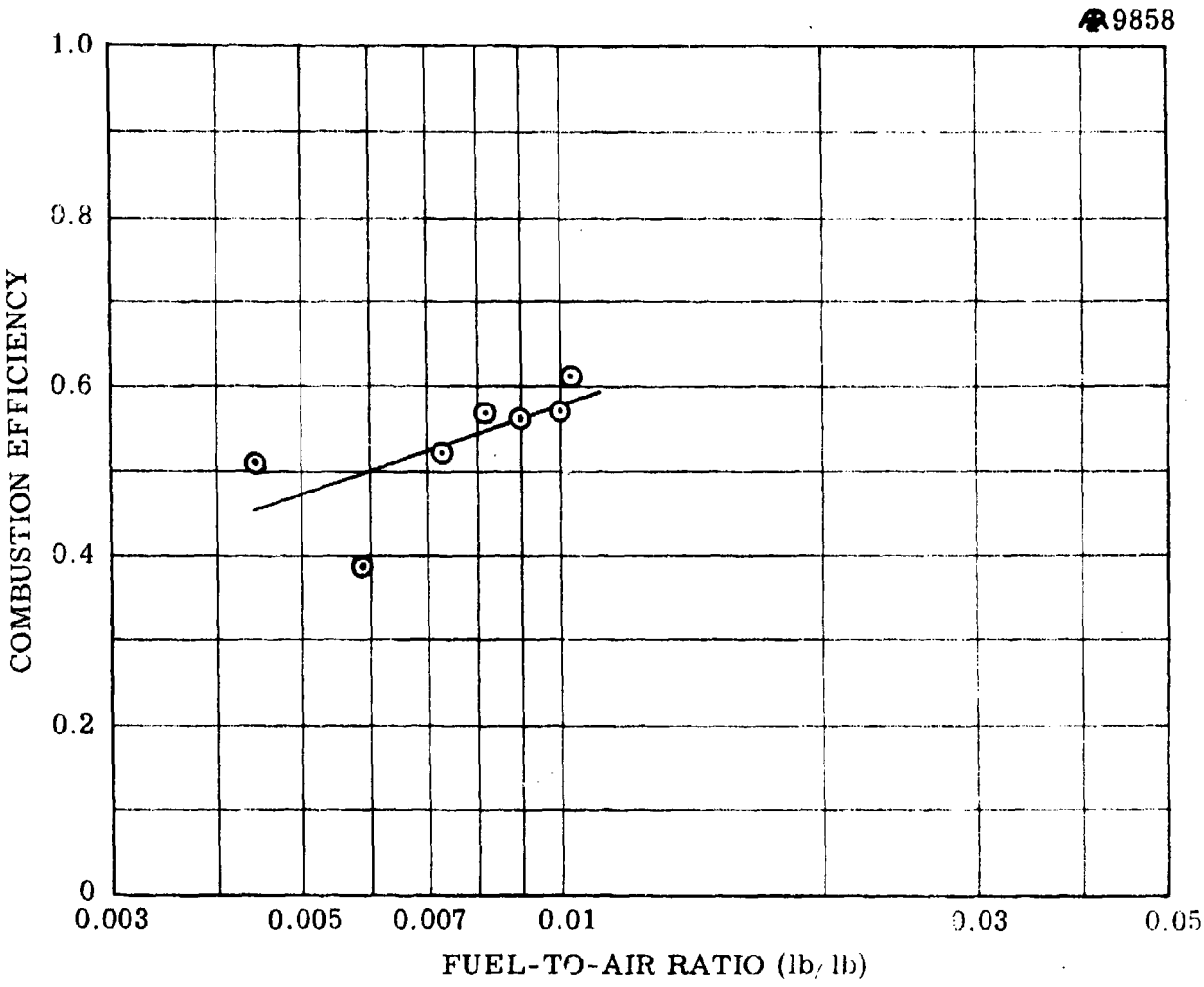

Figure 67. Results of Micro-Ramjet Test No. 35, Using Neat JP-4 as the Fuel. Inlet Conditions Mach 2.5, Sea Level, Cold Day. Dual-Fluid Injector Air Pressure 500 psig.

The fuel-to-air ratios of about 0.004 and 0.01 represent the lean and rich limits (respectively) of JP-4 combustion in the micro-ramjet under the conditions used in Test 35.

4.5.3.13 Tests 36 through 40

Tests 36 through 40 compared the combustion performance of various isopropanol-based boron slurries. Solids loadings of 50 to 75 per cent were used. The diffuser tube used in these tests was that shown in Figure 65 and 66, except that the metal fins at the rear of the shroud (used to provide a rotational moment to the primary fuel-air mixture) were removed.

Slurry formulations used in these tests and general results are presented in Table XXX. Combustion efficiencies from Tests 37 and 40 are plotted as a function of fuel-to-air ratio on Figure 68.

The combustion in all of the combustion tests in this series was very ragged, with sudden bursts of exhaust flame alternating with partially burned exhaust. It is believed that the conditions set by the diffuser were not conducive to good combustion of these slurries. This is also indicated by the significant peaking in combustion efficiency at a fuel-to-air ratio of about 0.0075 on Figure 68.

The flow problem of test 36 was due to the extremely cold (15°F) ambient condition. In subsequent tests this difficulty was overcome by applying heat (up to 120°F) to the slurry feed line and the ram body. This procedure allowed very high flow rates to be attained.

4.5.4 Discussion of Combustion Test Results with Dual-Fluid Injection

4.5.4.1 General Discussion

The most important results obtained from the tests using the

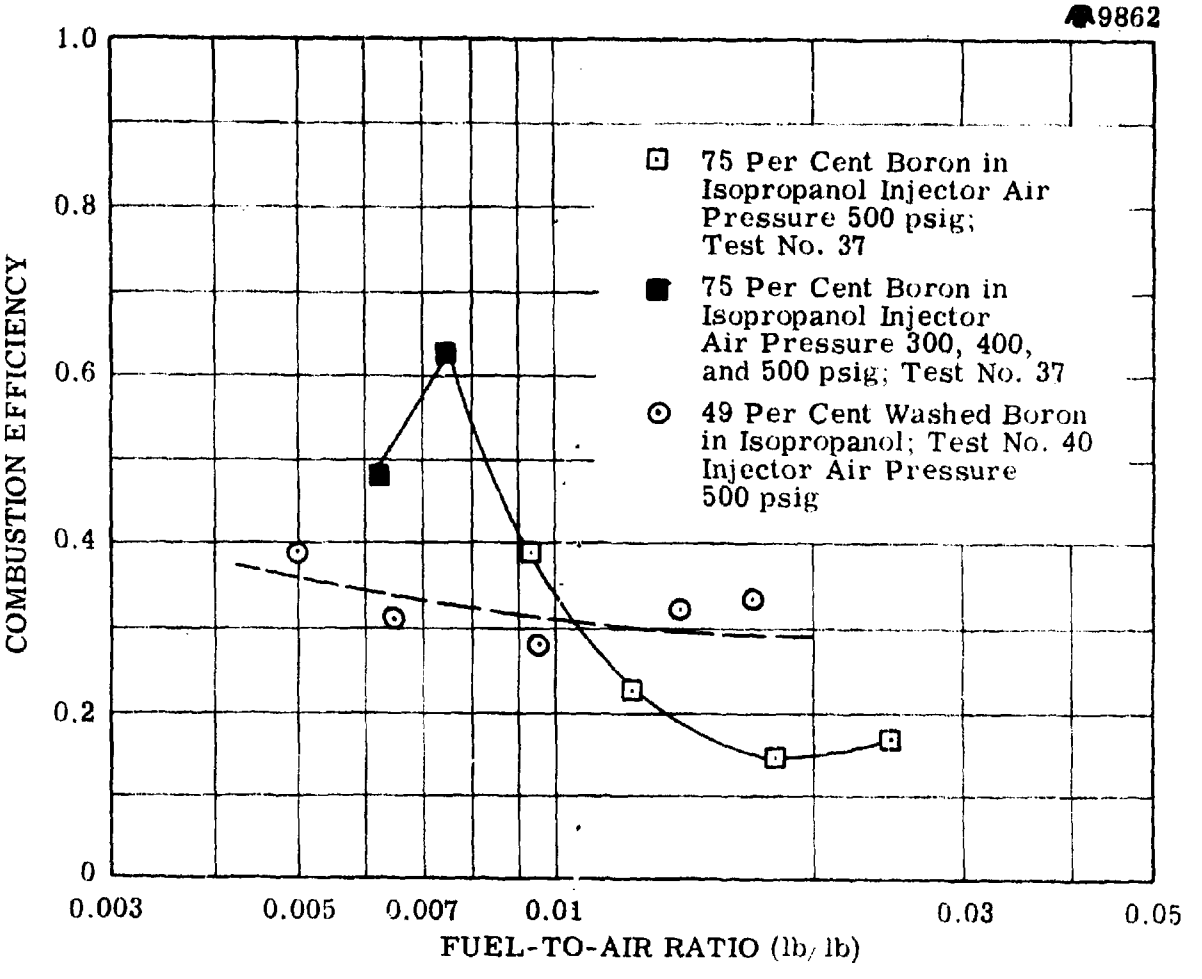

Figure 68. Results of 3.5-inch Micro-Ramjet Tests 37 and 40 for Two Isopropanol-Based Boron Slurries at Inlet Conditions of Mach 2.5, Sea Level, Cold Day, with Dual-Fluid Injection.

dual-fluid injector are summarized as follows:

(1) For efficiently atomized slurries of boron, the elemental particle size showed the strongest influence on combustion efficiency of any formulation variable tested.

(2) Combustion of boron dust clouds appears to be fairly sensitive to local mixture ratios, and quenching of the boron flame (either by a sudden change in mixture ratio or by removal of an ignition source) can be easily effected.

(3) In a finely atomized state, boron dust clouds will burn almost as completely as will atomized JP-4, for the conditions used in the micro-ramjet tests.

No relative ranking of all of the slurries tested with the dual-fluid injector can be made, but the comparison of three formulations (commercial grade, submicron, and ultra-fine types of boron) on Figure 64 appears to be valid, even though slightly different diffuser designs were employed.

Exhaust product sampling produced results in agreement with thrust-derived values for some tests (Test 23, Figure 63), but not in others (Test 25, Figure 63). Since the chemical values of combustion efficiency generally tended to be lower than thrust-derived values, it is believed that the sampler head was positioned in a fuel-rich central core of the flow-stream for these tests.

Slurry buildup was much less severe with the dual-fluid injector than with the particle mill, and no burnthroughs of the diffuser tubes occurred. Typical values of burner drag coefficient were unity for the dual-fluid injector plus diffuser and [illegible] to [illegible] for the

particle mill-burner can combination of Tests 1 through 15.

4.5.4.2 Particle Size Effects

The effect of primary boron particle size on combustion performance between tests 21, 26 and 27 correlates well with observations of the relative particle sizes collected in the exhaust samples for these three types of boron. For the ultra-fine, high purity boron, which exhibited the best combustion performance, the particles in the exhaust samples required twelve hours or more to agglomerate and settle to the bottom. It appeared that some of the particles were permanently suspended in the water. For the slurry of commercial grade boron, the particles agglomerated and settled to the bottom within two hours after collection. Photomicrographs of these particles before agglomeration (on a slide prepared within 15 minutes after collection) indicated that all of the particles collected were one micron or less in diameter. These particles, shown on Figure 69, agglomerated into loose chains of particles which resemble single particles of very high surface area in the photographs.

The submicron boron slurry produced large agglomerates, up to 1/32-inch in diameter, in the exhaust samples. These agglomerates settled out immediately, and the remainder of the boron particles in the samples required several days to settle out completely. The presence of the large agglomerates appears to be the reason for the relatively poor performance of slurries made with this type of boron. As was mentioned previously, the large agglomerates present in the slurries made with submicron boron must have resulted from the ball-milling process, but there is no explanation for the inability to completely disintegrate this type of boron into primary particles, since this was obviously accomplished with the ball-milled commercial grade boron.

The absence of any boron particles above one micron in diameter

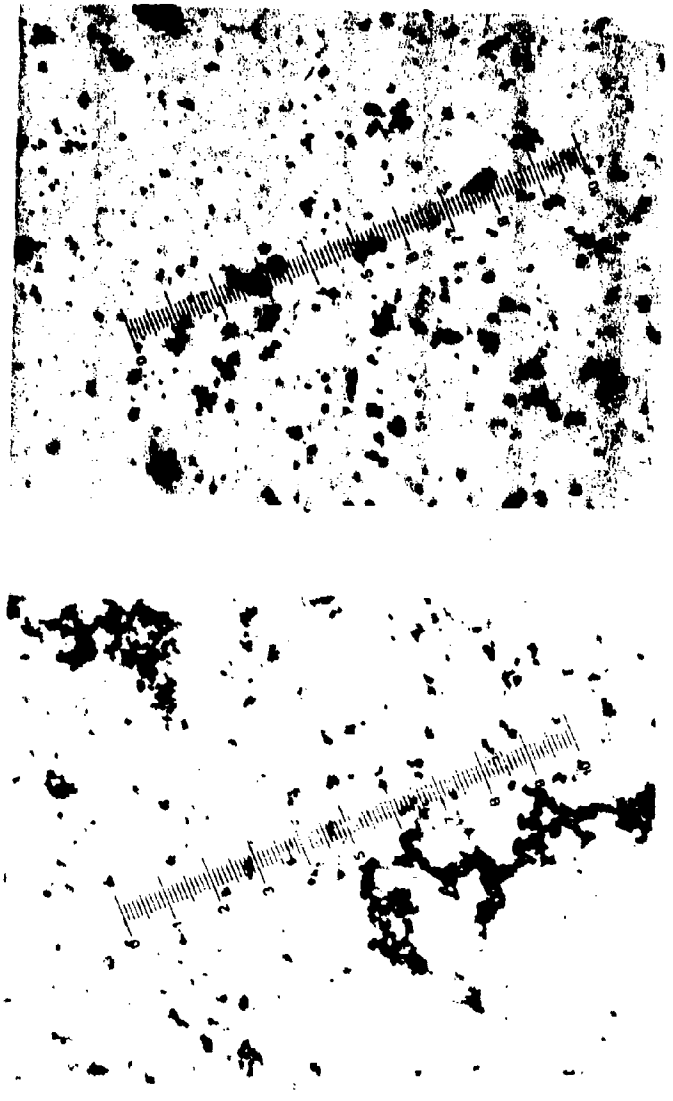

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Figure 69. Photomicrographs of Boron Particles Collected in Exhaust Samples During Combustion of a Slurry of 73 Per Cent Ball-Milled, Commercial Grade Boron in JP-4 (Test No. 23) in the 3.5-inch Micro-Ramjet with Dual-Fluid Injection (Injector Pressure 500 psig). Scale on the Photographs - 1.08 Microns per Small Division.

in the exhaust stream of a slurry containing ball-milled commercial grade boron which is burning at 30 to 50 per cent combustion efficiency suggests the hypothesis that considerable atomization of agglomerated particles can occur in the combustion zone. If this were correct, then the primary method of slurry atomization may not be as important to efficient combustion of boron slurries as had been expected. The mechanism of this "secondary" atomization (breakup of agglomerated particles) in the combustion zone could involve melting or vaporization of the material causing particle adhesion, which is believed to be oxides of boron, water, and other impurities.

5.0 BORON SLURRY TRADE-OFF CRITERIA

5.1 COMBUSTION PERFORMANCE

Fuel properties which may be expected to directly affect combustion performance include type of carrier, solids loading, type of boron and boron processing used, type and concentration of wetting agent, type and concentration of gellant, rheological properties, and the type and concentration of additives for enhancing ignition or combustion. Various aspects of the combustion process, such as optimum air distribution (optimum burner can design), provisions for flame holding, optimum L^*, and atomization efficiency may also be affected by one or more of the above formulation factors.

The determination of trade-offs between slurry properties and combustion performance is a complicated and difficult procedure. To date, combustion testing has included only a few fuel formulations tested with a restricted range of burner geometries and methods of atomization, and from these tests very little information pertaining to the various trade-offs between fuel properties and combustion is available.

Most of the effects of formulation variables on combustion appear to have been masked in the ramjet tests made to date with slurry fuels, although the following trends have been noted:

(1) The smaller the boron particles in the slurry, the more complete is the combustion;

(2) Increased carrier volatility appears to improve slurry combustion;

(3) The zone of most intense reaction in the burner appears to have an equivalence ratio near unity; for "more active" (in the ambient pressure combustor) slurries, the reaction appears to be more sensitive to local mixture ratios than other slurries.

The use of a more efficient atomizer (i.e., the dual-fluid injector) was expected to relieve some of the masking of formulation effects

which are believed to occur with the particle mill system. However, it appears that the trends listed above, except for the carrier volatility effect, apply to the dual-fluid injector as well.

Of the slurry formulations in the solids-loading range of 70 to 75 per cent tested in this program the most promising are 73 per cent ball-milled boron in isopropanol, and 70 per cent (ball-milled) high purity, ultra-fine boron in ungelled JP-4. The formulation with ultra-fine boron can be eliminated at present because of a higher relative cost and negligible enhancement of combustibility with particle mill atomization; but it should be considered in the future if more efficient methods of atomization are developed. Slurries containing 80 per cent solids possess undesirable rheological properties at high shear rates and/or low temperatures, and slurries containing 65 or less per cent solids are unattractive because of their lower theoretical volumetric heat releases.

5.2 TRADE-OFF AREAS INVOLVING CARRIER TYPE

Four types of carriers have evolved as the most promising, based on micro-ramjet and ambient pressure combustion tests and data on available solids loadings at low viscosities. The four (JP-4, isopropanol, isooctane, and methyl isobutyl ketone) all are volatile liquids which are readily available at low cost and present no significant toxicity or compatibility problems.

For a given solids loading, the type of carrier used is expected to affect rheology, storage stability, and combustion performance. Thus far, however, significant differences in combustion performance among slurries containing various carriers have not been established. In terms of storage stability of the slurries, isooctane appears to be a poor candidate. Even slurries loaded to 85 weight per cent solids in gelled isooctane have exhibited separation after a few weeks of shelf storage. The reasons for this instability are probably the low density of the liquid and the relative compactness of the molecule (leading to poor interaction with wetting agents and gellants). Isooctane is also the most volatile of the four candidates, and, because of this, requires extreme care in formulation

and storage to insure the desired solids loading. Another potential problem with isooctane is the tendency of highly loaded isooctane-based slurries to become dilatant at shear rates lower than those for other types of formulations.

Methylisobutyl ketone (MIBK) offers high solids loadings in a solvated system (no gellant required), but MIBK-based slurries appear to be relatively unstable at solids loadings below about 82 per cent. Combustion testing of MIBK-based slurries in the micro-ramjet have not been successful, but these slurries appeared promising on the basis of results obtained with the ambient pressure burner.

Isopropanol and JP-4 have been the carriers of greatest interest during the past several years. JP-4 requires a gellant for slurry storage stability, whereas isopropanol does not. In this program, slurries made with these two carriers exhibited very similar combustion performance in the micro-ramjet test engine equipped with a particle mill injector.

Three of the four carriers are compared on the basis of theoretical volumetric heating value on Figure 70. Slurries made with MIBK carrier would produce volumetric heating values between those for isopropanol and JP-4. The curve for the high-purity boron in JP-4 represents the limit of volumetric heating value improvement available through the use of a pure boron powder.

On the basis of Figure 70, there are no significant differences among the heating values for slurries formulated with the various carriers at a given solids loading which could not be compensated for by either a slight enhancement of combustion efficiency or the improvement of some other critical property. The difference between the lowest heating value (for isooctane) and the highest (for JP-4) is less than five per cent at all of the solids loadings shown on Figure 70.

Most of the comparisons made in subsequent paragraphs of this report will be between JP-4-based slurries and isopropanol-based slurries. These two general formulations not only represent the two general types of slurries available (gelled systems and solvated systems, respectively),

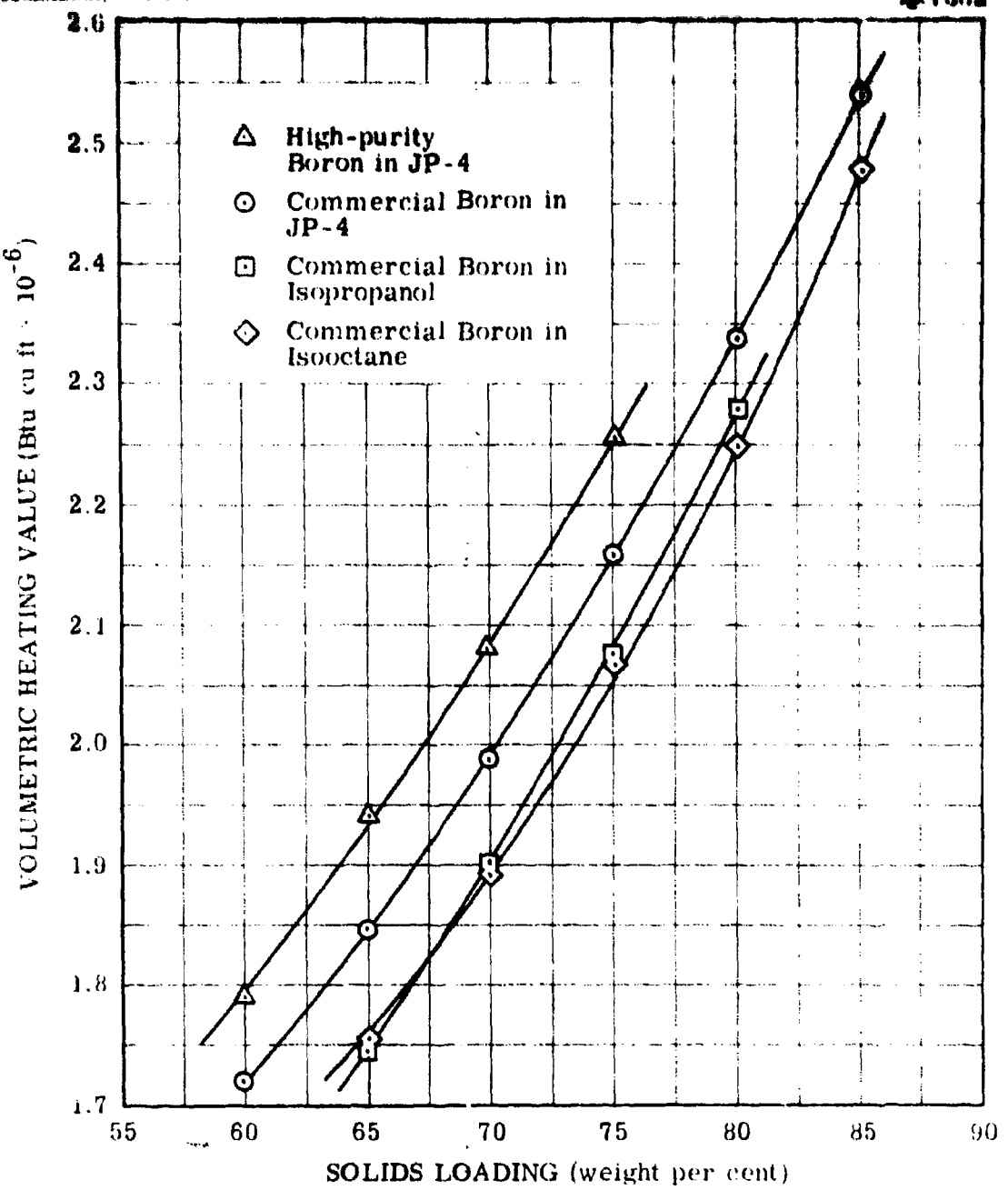

Figure 70. Theoretical Volumetric Heat Release Versus Solids Loadings for Slurries of Boron in Three Carriers at 70°F (Heating Value of Commercial Boron 3.5×10^6 Btu/cu. ft., All of Liquid Phase Assumed to be Carrier).

but they are also considered much more promising on an overall basis than the other two candidates.

5.3 TRADE-OFFS INVOLVING SOLIDS LOADING

A solids loading of 73 to 75 per cent has been used for most boron slurry work to date. Typical values of Btu/Cu.Ft. for JP-4 and slurries of 73 per cent commercial boron in JP-4 and isopropanol are as follows (volumetric heating values for other solids loadings can be determined from Figure 70):

Fuel	$Btu/Cu.Ft_\delta \times 10^{-6}$ at $70^\circ F$	Relative Figure of Merit
JP-4	0.87	1.00
73% boron in JP-4	2.09	2.40
73% boron in isopropanol	2.01	2.31

Although a solids loading of about 73 per cent probably represents a minimum desirable value, a lower limit on solids loading cannot be established at present because of possible conflicts with rheological and combustion performance considerations at low temperatures. If low viscosities at temperatures in the region of $-65^\circ F$ are mandatory, then the optimum solids loadings will shift toward lower values for either type of slurry. It is possible that the effects of such low temperatures on slurry atomization and subsequent combustion will be important, in addition to their effect on slurry transfer.

A solids loading of 80 per cent appears to be a reasonable maximum since it is at approximately this loading (with ball-milled boron) that dilatant tendencies begin to appear in hydrocarbon-based slurries. For the isopropanol-based slurries, a loading of 80 per cent solids appears to be the maximum attainable at reasonable viscosities, regardless of whether ball-milled boron or a bimodal mixture of washed boron powders is used. However, for either general type of slurry, improved particle size distributions must be available in order to meet low-temperature rheological specifications, at 80 per cent solids.

In general, storage stability is enhanced by increased solids loading for either type of slurry (JP-4 or isopropanol carrier), but for both types sufficient stability over a two-year storage period appears to be available for the range of 73 to 80 per cent solids. Lower loadings could probably produce stable formulations if close control of boron processing and formulation variables could be maintained.

5.4 RHEOLOGICAL FACTORS

Desirable properties for boron slurry fuels include the following three rheological factors:

(1) A yield stress high enough to enhance storage stability but not large enough to interfere with pump start up or other transfer system behavior;

(2) Pseudo-plastic or Newtonian behavior over a shear rate range of 50 sec^{-1} to about 100,000 sec^{-1};

(3) Minimum apparent viscosity over the entire shear rate range.

A fourth property, that of minimum increase in viscosity as temperature is decreased, may also prove to be desirable due to the goal of 400 poise maximum apparent viscosity at a shear rate of 100 sec^{-1} and a temperature of -65°F.

Gelled slurries (those with hydrocarbon carriers such as JP-4 or isooctane) at solids loadings approaching 80 per cent generally exhibit pseudo-plasticity (viscosity decreasing with increasing shear rate) over a portion of the shear rate range and become dilatant (viscosity increasing with increasing shear rate) at some value of shear rate which is dependent on the solids loading and the temperature. Solvated slurries (those with polar carriers such as isopropanol or MIBK) have, thus far, shown no tendency toward dilatancy over the shear rate range covered by our capillary viscometry work (up to 40,000 sec^{-1}).

Low temperature rheology data for two "standard" formulations,

73 per cent ball-milled boron in JP-4 (4 per cent gellant), and 75 per cent ball-milled boron in isopropanol, indicate that the effect of temperature on viscosity is severe. Representative viscosity data at -65°F for these slurries, both of which appear to be shelf-storable without separation, is shown on Table XXXI.

Slurries of both general types containing 80 per cent solids appear frozen at -65°F. The values of viscosity at low temperatures may be improved by various methods. For the JP-4-based slurry at 73 per cent solids, a more effective gellant requiring only about 0.25 per cent of the total by weight may be available, and for the isopropanol-based slurry, removal of surface water may result in lower viscosities with no sacrifice in other rheological properties or storage stability.

The effects of slurry rheological properties on atomization and combustion are not known, and are expected to vary with different methods of atomization. It is expected that different rheological properties of various slurries will affect the efficiency of the atomizer. Dilatant slurries, for example, might be expected to result in a greater atomization efficiency in the particle mill, therefore producing smaller particles in the flame zone and thereby enhancing combustion efficiency. Effects of the requirements of fuel expulsion and pumping on rheological criteria can be defined to a certain extent, and are still under study. It is believed that the criterion of 400 poise viscosity (or less) under the worst temperature conditions is reasonable for centrifugal pumps, but may be more stringent than necessary for simple transfer up to the pump. It may not be necessary that the storage temperature and the temperature of the slurry in the pump (or at the atomizer) be the same, since an abundance of heat could be made available from the boost phase of a projected missile for increasing the slurry temperature in transit by the time the ramjet phase is initiated. Preliminary calculations have indicated that the slurry temperature could be raised by as much as 150°F between the storage area and the injector through the use of standard methods (such as finning the transfer tube) to increase the heat transfer rate.

TABLE XXX

TYPICAL VISCOSITY RANGES FOR BORON SLURRIES IN JP-4 AND ISOPROPANOL AT ROOM TEMPERATURE (70°F) AND -65°F

Slurry	Apparent Viscosity at 70°F poise		Apparent Viscosity at -65°F, poise
	100 sec^{-1} shear rate	10,000 sec^{-1} shear rate	100 sec^{-1} shear rate
73% Ball-Milled Boron in JP-4 (0.99% gellant)	50 - 100	10 - 30	~5,000
75% Ball-Milled Boron in Isopropanol	150 - 200	10 - 20	~4,000

Where a centrifugal pump is used, it is necessary to retain pseudo-plastic or Newtonian characteristics of the slurry up to fairly high shear rates, on the order of 100,000 sec^{-1}, to insure proper pump operation. Outside of the pump the shear rates attained in any transfer system will probably be less than 1,000 sec^{-1}, and dilatancy should not be a problem if solids loadings are kept below 80 per cent.

5.5 BORON PROCESSING

The only method identified to date for achieving a solids loading of 80 per cent in a hydrocarbon carrier at usable viscosity levels is through the provision of a particle size distribution by agglomerating single particles of commercial boron. Most of the work in this area has involved ball-milling, but this process results in oxidation of some of the boron and the formation of some large particles which probably will not burn efficiently. Boron slurries of 73 per cent solids in hydrocarbon carriers have been prepared both by "overload dilution" during the mixing operation[2] and through breaking up of agglomerates in as-received commercial boron ("multimodal milling")[8] but usable slurries prepared by these methods above 73 per cent solids have not been reported.

It has been demonstrated on this program that solids loadings in the range of 73 to 80 per cent are possible for isopropanol-based slurries both as a result of ball-milling of the boron and from blending of bimodal particle size distribution of isopropanol-washed boron powders. Washing and drying, followed by mixing (with either carrier), has not proved successful mostly because of reproducibility problems, but slurries made by this method have shown combustion properties similar to (or better than, for low solids loadings) slurries containing ball-milled boron.

Neither the effect of washing the boron to remove oxide impurities nor the effect of ball-milling on combustion performance of the slurries is well understood. It is believed that these effects have, in the past, been masked somewhat by inefficient slurry atomization. Although directly comparative data are few, the data that are available have suggested that all slurries of the same general composition (same carrier and same solids

loading) will perform similarly in a ramjet engine.

5.6 STABILITY CRITERIA

5.6.1 Hydrocarbon-Based (Gelled) Systems

Storage stability for two years is a reasonable requirement for boron slurry fuels. It has been demonstrated that shelf lives of two or more years are possible with both gelled slurries (JP-4 carrier) and solvated systems (isopropanol carrier). The isopropanol-based slurries are generally more stable than the gelled systems at comparable loadings, probably because of the wetting agent-gel interactions which can occur in hydrocarbon-based slurries. This type of interaction is demonstrated by the addition of wetting agent to the gel (prior to mixing), which completely destroys the gel structure. Addition of boron to the gellant-wetting agent solution removes a portion of the wetting agent to the surface of the boron and thus allows some gel reformation. Gel reformation is the source of the yield stress, stability to settling, and pseudo-plastic rheological behavior of the hydrocarbon-based slurries!

Once the wetting agent concentration is set (usually at about three per cent of the solids concentration), the apparent viscosity (and other rheological properties) and the stability of the slurry formulation are determined largely by the type and concentration of the gellant. A typical example of a trade-off of stability to centrifugation versus apparent viscosity at various temperatures, based on the variation of gellant concentration over what is considered a practical range, was presented for a "standard" slurry formulation in Table II. It has been found that slurries which show separation of less than about four per cent in the centrifuge test (at 750 "g" for 24 hours) will be stable to separation in shelf storage for long periods of time. If the type or concentration of wetting agent were varied from that used for the slurries described on Table II, a new set of numbers would apply, tending towards higher viscosities (and, generally, greater stability) regardless of whether the concentration was increased or decreased or what new type of wetting agent was used.

It has been found from experience in mixing large batches of hydrocarbon-based slurries (up to 450 pounds per batch) that neither the shear stress-shear rate curve nor the storage stability of a given gelled formulation can be closely reproduced. The primary reason for the difficulties encountered in reproducibility appears to be inconsistency in the results obtained from ball-milling of the boron prior to formulation in the mixer. The effects of ball-milling vary somewhat with the moisture content of the powder, the amount of oxidized material present, and the cleanliness of the mill and its charge of balls. Of course, the milling effect is a strong function of the milling time and total charge, but these can be reproduced much more precisely than the other variables associated with the process. The use of ball-milling or any other type of processing to achieve high solids loadings at low viscosities in a boron slurry through agglomeration of primary particles is considered undesirable. Not only are these processing steps very difficult to control and reproduce, but they also lead to larger slurry particles during subsequent atomization.

Mixing procedure is also believed to contribute to the observed non-reproducibility of boron slurry batches. For example, addition to the batch of slightly dried slurry from the blades and walls of the mixer appears to result in "lumps" in the slurry; it thus appears that the gelled slurries cannot be homogenized by diffusion processes during storage.

Most hydrocarbon-based slurries show aging, or increases in viscosity with time, during storage. The major portion of the aging process is completed within a few days after slurry manufacture. It is for this reason that apparent viscosities are measured after the slurries have been allowed to age at least overnight. According to our present knowledge, aging is caused by the adsorption of wetting agent onto the porous surface of the boron during storage, resulting in the formation of additional gel structure in the carrier. It is probably for this reason that hydrocarbon-based slurries which separate do so within the first few months of storage.

Hydrocarbon-based slurries also exhibit significant density re-

ductions during storage due to hydrogen formation at the boron surface. Removal of surface water can probably prevent these density changes.

5.6.2 Isopropanol-Based (Solvated) Systems

Isopropanol-based boron slurries appear generally more stable to separation during storage than their gelled, hydrocarbon-based counterparts. In addition, the solvated slurries have exhibited no aging over a storage period of six months, are more reproducible even though ball-milling may be used, and may not exhibit sensitivity to a critical container diameter for separation during storage. All of these properties are consistent with the present knowledge of the type of structure which is present in the slurry. In solvated slurries, the structure is formed through the chemical interaction of carrier with the boron. Hydrogen bonding and perhaps other types of close-range interactions are believed to be involved. Whatever the specific bonding mechanisms may be, they do not appear to produce any net chemical changes in the system except, possibly, at the surface of the particles. These bonds are presumably instantaneous (therefore, no aging) and appear to be homogeneous throughout the system (therefore, the possibility of no critical storage diameter). The greater stability of these systems in comparison to hydrocarbon-based systems probably results from the fact that the entire carrier is affected (enters into the structure) and not just the portion in which wetting agent-gellant interaction is insufficient to prevent the gel breakdown, the case which occurs in hydrocarbon-based systems.

It is interesting to note that the ultra-fine boron powders form slurries with JP-4 which require no gellant. These slurries may be comparable to other slurries containing very small particles (such as carbon black slurries or colloidal suspensions), or, perhaps, there is enhanced particle-carrier chemical interaction of some sort. Based on shelf-storage tests to date, these slurries also appear to be generally more stable than the gelled systems containing an agglomerate size distribution of commercial grade boron.

For isopropanol-based slurries, there is probably a critical solids loading below which settling occurs and above which no settling occurs. The settling for this type of system is rapid, if it occurs at all, because it results from there being more carrier present than the maximum which can interact with the boron surface and/or alcohol molecules near the surface of the particles to form a continuous structure. For as-received commercial boron, the minimum solids loading above which settling will not occur is probably about 65 per cent. With ball-milled boron it is expected that about 73 per cent solids is the minimum stable loading, and this is probably a good estimate of the minimum stable loading for a bimodal distribution of washed commercial boron and ultra-fine boron powders. All of these loading limits are based upon slurries in isopropanol.

Above the minimum solids loadings, all of these slurries appear completely stable under shelf-storage conditions. In the case of isopropanol-based slurries, it may be possible to enhance both stability and rheological properties through vacuum drying of the ball-milled material to remove volatile impurities such as boric acid and water. These slurries (and, in fact, all boron slurries) should be stored in an inert atmosphere to prevent oxidation at the surface of the slurry.

5.7 ADDITIVES

Additives have thus far provided no tangible benefits to boron slurry combustion performance in terms of Btu/cu.ft. delivered. At present, only one additive, fluorine gas, appears to be a promising candidate for the enhancement of slurry combustion efficiency without excessive loss of volumetric heating value. This is based on the work reported in Reference 9, in which fluoride compounds were used to promote boron combustion in a DTA apparatus.

6.0 CONCLUSIONS

The following conclusions are based on the results and observations obtained from this program:

(1) Through ball-milling of the boron (or, possibly, other agglomeration procedures), slurry fuels containing high purity, ultra-fine or submicron boron powders can be formulated at solids loadings sufficient to be competitive with presently used formulations containing commercial boron, in terms of theoretical volumetric heat release;

(2) The degree of separation under centrifugation at 750 g for 24 hours can be used as a relative measure of stability to phase separation of gelled boron slurries during shelf storage;

(3) Slurries of ball-milled commercial-grade boron contain a continuous particle size distribution of about one to fifty microns in diameter, with a weight-average mean diameter of about twenty microns;

(4) JP-4-based boron slurries atomized in the particle mill produce mostly particles in the size range of 25 to 100 microns, and some particles much smaller and much larger than this range;

(5) Of the atomization methods tested, a poppet atomizer using slurry heated to above the boiling point of the carrier and pressurized to 500 psig, produced the most effective slurry atomization;

(6) In the 3.5-inch micro-ramjet test series with particle-mill injection, good qualitative agreement was obtained with previous Marquardt test results obtained with a 6.3-inch test engine. This agreement establishes a base line for the use of the micro-ramjet in evaluating the combustion performance of experimental slurry fuels;

(7) Correlations of slurry properties with combustion performance obtained from the micro-ramjet test series were as follows:

(a) Increased volatility of the carrier enhanced combustion performance;

(b) Smaller particle sizes resulting from atomization enhanced slurry performance;

(c) Removal of surface contaminants may have enhanced boron combustibility;

(8) The combustion efficiency of the liquid carrier was approximately that of the boron in most of the micro-ramjet tests;

(9) Combustion of boron dust clouds does not appear to be piloted by ignition of vaporized carrier, under the conditions used in the micro-ramjet tests;

(10) With the dual-fluid injector, the only slurry property which significantly affected combustion was the primary particle size of the boron;

(11) Combustion of boron dust clouds appears to be sensitive to local mixture ratio, and quenching of the flame (either by a large change in local mixture ratio or removal of an ignition source) is rather easily effected;

(12) At present, the most critical trade-off among properties of boron slurry fuels is between storage stability and rheological properties (viscosity and yield stress) at low temperatures;

(13) Of the slurry formulations studied under this program, the most promising are as follows:

(a)	73.00%	ball-milled, commercial grade boron
	2.19%	glycerol sorbitan laurate wetting agent
	0.99%	modified polystyrene gellant
	23.82%	JP-4
	100.00%	

and

(b)	75.00%	ball-milled, commercial grade boron
	2.25%	n-octylamine wetting agent
	22.75%	isopropanol
	100.00%	

These slurries exhibited very similar combustion performance in the micro-ramjet tests with particle mill injection.

7.0 RECOMMENDATIONS

The following recommendations are made on the basis of the results and observations obtained from this program:

(1) It is recommended that redirected development of boron slurries be undertaken to meet the stringent demands of viscosity and yield stress criteria at low temperature (yield stress less than 12 lb/sq. ft., apparent viscosity less than 400 poise at 100 sec^{-1}; both at -65° F);

(2) It is recommended that methods of eliminating or minimizing undesirable aging effects in boron slurries be developed. These effects include gas formation and increases in yield stress and apparent viscosity during storage;

(3) It is recommended that methods of obtaining boron particle size distributions in the diameter range of one to fifty microns, without the use of ball-milling or other agglomerating techniques, be developed;

(4) It is recommended that basic information on combustion of boron dust clouds in air, including flammability limits, effective flame velocities, quenching distances, particle size effects, etc., be obtained to aid in development of slurry combustors;

(5) It is recommended that several phases of research on boron slurry combustion in the micro-ramjet engine be continued, especially definition of the effects of varying inlet air temperature, determination of effects of local mixture ratios, investigation of the role of radiation from the burner walls in ignition of boron particles, and further research into the extent of atomization which may occur in the combustion zone;

(6) It is recommended that the removal of contaminants from the boron surface be further investigated as a possible method

of enhancing boron combustion;

(7) It is recommended that a poppet-type atomizer, in combination with a regeneratively heated slurry feed system, be considered as a promising method of obtaining a low velocity stream of finely atomized boron (slurry) particles for injection into the combustion zone of a ramjet engine.

8.0 REFERENCES

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APPENDIX I

GLOSSARY OF

TRADENAMES AND MANUFACTURERS

TABLE XXXI

GLOSSARY OF TRADENAMES

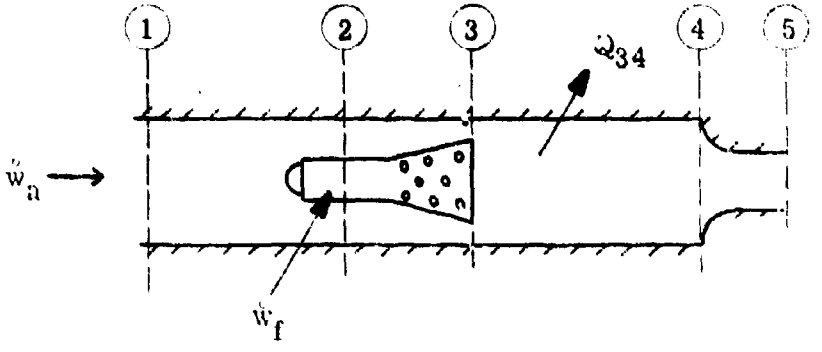
AND MANUFACTURERS

Type of Material or Equipment	Trade Name	Manufacturer
Boron		
Commercial grade boron	--------	American Potash and Chemical Co.
Submicron boron	--------	AVCO Corporation
High purity, ultra-fine boron	--------	Callery Chemical Co.
Gelling Agents		
Aluminum soap	Alumagel	Witco Chemical Co.
Modified (or substituted) polystyrene	X-3487-427-21A	Dow Chemical Co.
Aluminum salt	AlMB-2	Shell Development Co.
Wetting Agents		
Amine surfactant	Duomeen RO	Onyx Chemical Co.
n-Octylamine	Armeen 8D	Armour and Co.
Glycerol sorbitan laurate	Atlas G-672	Atlas Powder Co.
Equipment		
Rotating viscometer	Rotovisko	Haake Instrument Co.
Ultrasonic (or Hartmann whistle) nozzle	Astrospray	Astrospray Corp.

APPENDIX II

ESTIMATION OF RAMJET COMBUSTION EFFICIENCY BY MEANS OF JET THRUST

Several basic techniques can be employed to determine ramjet combustion efficiency. The exhaust products can be directly subjected to chemical analysis and the total pressure of the exhaust stream can be measured. For the slurry fueled ramjet having a polyphase exhaust stream with a nonhomogeneous solid/liquid phase distribution, pressure measurement and exhaust sampling present problems. Combustion efficiency obtained by measuring jet thrust circumvents many of these difficulties and performance can be determined by the following procedure. Given a ramjet configuration as shown in the schematic below:



Air metered by a flow rate control system is delivered to the ramjet burner can and mixed with boron slurry fuel. The fuel slurry is dispersed and the slurry vehicle vaporized between Stations (1) and (2). Between Stations (2) and (3) combustion occurs and the exhaust products move down the exhaust duct to Station (4) where they exhaust to the atmosphere at Station (5) in a "Mach 1" or sonic free jet. The walls of the exhaust duct remove heat from

the combustion products at a rate denoted Q_{34}. The heat removed is measured by determining the temperature rise in the exhaust duct cooling water.

In order to place the combustion efficiency to be evaluated in meaningful context, a chemical model of the combustion process must be given. Inasmuch as the exhaust gas temperatures are for the most part low, $T_{t_5} < 3000°F$, an elementary chemical model is employed.

$$\alpha_0 B + \alpha_1 C_x H_y O_z + \alpha_2 O_2 + \alpha_3 N_2 + \alpha_4 A \rightarrow$$
$$\beta_1 B + \beta_2 B_2 O_3 + \beta_3 H_2 O + \beta_4 CO_2 + \beta_5 O_2 + \beta_6 N_2 + \beta_7 A \qquad (1)$$

It is assumed that the metal fuel component, in this case boron, goes to its common oxide B_2O_3 and that the hydrocarbon vehicle oxidizes to CO_2 and H_2O. The cracked hydrocarbon species resulting from combustion inefficiencies are neglected in the product summations. The molal flow of reactants is given in forms of the weight flow of fuel and air and their respective composition weight fractions. In general, for reactants, the molal reactant flow is:

$$\alpha_i = \frac{k_i}{m_i} \dot{w}_j \qquad (2)$$

where

k_i = weight fraction
m_i = molecular weight
$\dot{w}_j$ = air/fuel flow rate

The molal flow of products is computed by the familiar conservation of atoms procedure. With the mols of reactants and products thus defined, the total enthalpy flow at Station (3), where combustion is assumed to be complete, is:

$$\dot{H}_3 = \sum_{i=0}^{n} \alpha_i h_i(T_j) + \eta\left(\alpha_0 \Delta H_{0_B} + \alpha_1 \Delta H_{0_{(CHO)}}\right) \qquad (3)$$

where

T_j - the initial fuel and air total temperature

η - the combustion efficiency

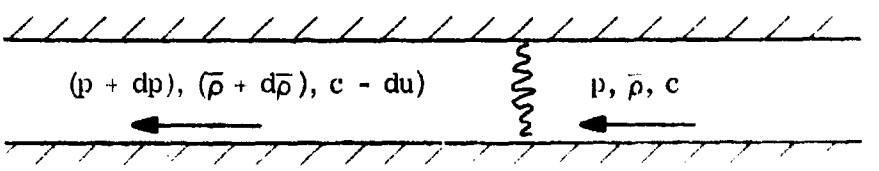
A temperature at Station (3) can be computed by determining at what total temperature T_{t_3} the product enthalpy summation will satisfy the equation

$$\mathring{H}_3 = \sum_{i=1}^{n} \beta_i h_i \left(T_{t_3}\right) \tag{4}$$

Moving to Station (5), the exit plane of the exhaust duct, the total enthalpy flow is the same as Station (4) which differs from Station (5) enthalpy by that heat given up to the exhaust duct cooling water. Thus, at Station (5), the total enthalpy flow is:

$$\mathring{H}_5 = \mathring{H}_3 - Q_{34} = \sum_{i=1}^{n} \beta_i h_i \; T_{t_5} \tag{5}$$

With the enthalpy thus defined for the exit plane, the procedure for estimating thrust follows directly from the assumption that the flow in the exhaust nozzle is an isentropic expansion of the combustion products to the sound velocity of the exit plane. For the polyphase flow conditions of the exhaust, where condensed phases of metal oxide appear as exhaust products, both kinematic and thermodynamic equilibrium are assumed to exist. In the case of boron, the oxide product phase is assumed to be liquid and the equilibrium second speed relationship can be developed in the following way. Given a stationary wave in a gas/dust mixture constrained to a constant area channel as shown in the sketch below:



where

p = pressure
$\bar{\rho}$ = composite density
c = gas velocity into the wave

The conservation equations of momentum and mass taken together result in an expression for the pressure differential through the wave in terms of the velocity differential.

$$dp = \bar{\rho}\, c\, du \tag{6}$$

The composite density can be expressed as

$$\bar{\rho} = (1 + \epsilon)\rho_g \tag{7}$$

Using the mass continuity equation across the wave to eliminate the velocity differential in the momentum equation and substituting for the composite density gives the relationship

$$dp = (1 + \epsilon)\, C^2\, d\rho_g \tag{8}$$

For infinitesimal pressure and velocity changes the process may be assumed adiabatic and reversible; thus

$$C^2 = \frac{1}{(1 + \epsilon)}\left(\frac{\partial p}{\partial \rho_g}\right)_s \tag{9}$$

Since for the isentropic wave there can be no change in entropy, application of the second law of thermodynamics and the equation at state for perfect gases gives the following expression relating pressure and volume

$$(\epsilon C_s + Cv_g)\frac{dp}{p} + (\epsilon C_s + Cp_g)\frac{dv_g}{v_g} = 0$$

which when integrated takes the famil ar form:

$$pv_g^{\,k} = \text{constant} \tag{10}$$

where

$$k = \frac{\epsilon C_s + Cp_g}{\epsilon C_s + Cv_g}$$

Using the modified ratio of the specific heats, the sound speed becomes

$$C^2 = \frac{k}{1+\epsilon} R_g T \tag{11}$$

where

R_g = gas constant of the gas phase alone

In the case where one or more gaseous and solid/liquid species are present, as in the exhaust of a ramjet combustor using metalized fuels, the sound speed can be given as

$$C^2 = \left(\frac{T}{\frac{\overline{m}'}{R} - \frac{1}{\overline{Cp}}} \right) \tag{12}$$

where

$$\overline{m}' = \frac{\Sigma \beta_i m_i}{\Sigma \beta_i'}$$

$$\overline{Cp} = \frac{\Sigma \beta_i Cp_i}{\Sigma \beta_i m_i}$$

and the prime denotes summation on the gas phase species only.

With the sound speed thus defined, the procedure for determining the static temperature and velocity at the exit plane requires an equation relating total enthalpy, static enthalpy and velocity. This relationship for the exit plane is

$$\frac{U_5^2}{2} = \mathring{H}\left(T_{t_5}\right) - \sum_{i=1}^{n} \beta_i h_i(T_5) \tag{13}$$

and, of course, the equivalent expression for sound speed is

$$C_5^2 = \frac{T_5}{\frac{\overline{m}_5'}{R} - \frac{1}{\overline{Cp}_5}} \tag{14}$$

For sonic conditions at the exhaust

$$U_5^2 \quad C_5^2$$

and both the exhaust static temperature and velocity are determined. The mean static pressure at the exhaust is calculated using the equation:

$$p_5 = \frac{R T_5}{A_5 K_E U_5} \sum_{i=1}^{n} \beta_i' \tag{15}$$

where the prime denotes gas phase products only. The discharge coefficient K_E is determined by calibration procedures which will be described further on.

The thrust of the ramjet test apparatus is now defined and can be expressed in terms of the quantities calculated thus far

$$F = \frac{U_5}{g} \sum_{i=0}^{n} \alpha_i m_i + A_5(p_5 - p_a) \tag{16}$$

where

p_a = atmospheric pressure

With the thrust so defined, it is now possible to converge the calculated thrust to the observed thrust by iterating on combustion efficiency. This is accomplished in practice by using a false position search procedure where zero efficiency and unit efficiency are used as the initial boundary values.

Having determined combustion efficiency, it is desirable to round out the process and compute a number of auxiliary parameters such as exhaust total pressure, combustor pressure loss coefficient and specific impulse. Of these, total pressure and combustor drag are the most laborious. The formula for computing total pressure in a gas-dust mixture where the species

have temperature dependent thermodynamic properties can be developed by assuming as before thermodynamic and kinematic equilibrium. Since total pressure results from the isentropic stagnation of a flow, setting the derivative of the entropy of the flow equal to zero is the obvious starting point.

$$\frac{dU + pdv_g}{T} = 0$$

By expanding the internal energy term and using the equation of state to eliminate the volume differential, the equation becomes:

$$\left(\frac{\sum_{i=1}^{n} \beta_i Cp_i}{R \sum_{i=1}^{n} \beta_i'} \right) = \frac{dT}{T} = \frac{dp}{p} \tag{17}$$

Integration and substitution of appropriate limits result in the equation:

$$\ln\left(\frac{p_{t_5}}{p_5}\right) = \frac{1}{R} \int_{T_5}^{T_{t_5}} \frac{\Sigma \beta_i Cp_i}{\Sigma \beta_i'} \frac{dT}{T} \tag{18}$$

which can be solved by numerical integration.

The combustor pressure loss coefficient is defined as

$$C_B \equiv \frac{p_{t_1} - p_{t_5}}{q_1} \tag{19}$$

where

q = the incompressible dynamic pressure

The computation of the dynamic pressure is all that is required to determine this coefficient. In terms of the measured total pressure at Station (1), the dynamic pressure is:

$$q_1 = p_{t_1} \frac{\gamma_1}{2} M_1^2 \left(1 + \frac{\gamma - 1}{2} M_1^2\right)^{\frac{\gamma_1}{1 - \gamma_1}} \tag{20}$$

where

γ_1 = ratio of the specific heats
M_1 = Mach number

The Mach number of the flow is determined by solving the equation

$$\frac{\overset{\circ}{w}_a \sqrt{T_{t_1}}}{p_{y_1} A_1} = M_1 \sqrt{\frac{\gamma_1}{R_1}} \left(1 + \frac{\gamma - 1}{2} M_1^2\right)^{-\frac{\gamma_1}{2(\gamma_1 - 1)}} \tag{21}$$

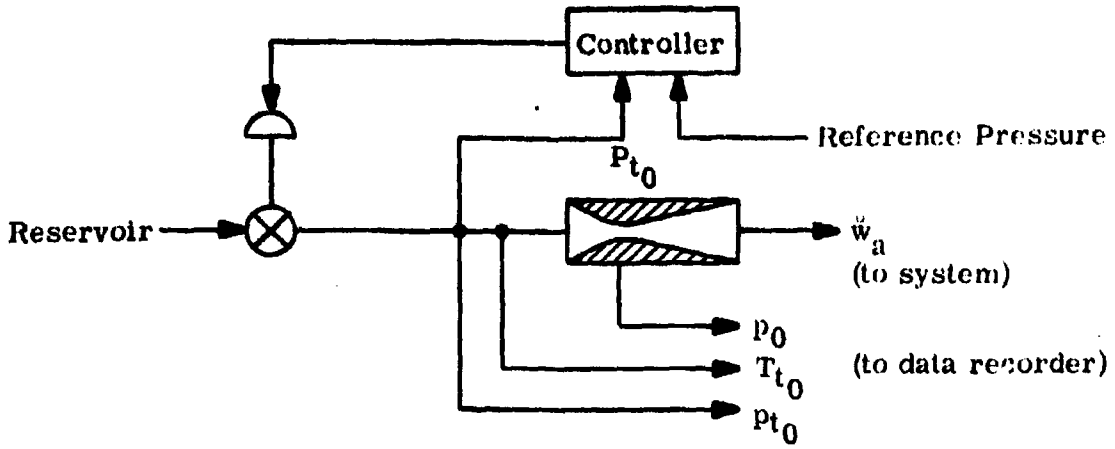
where

$\overset{\circ}{w}_a$ = weight flow of air

Specific performance can be expressed in any number of ways depending upon one's interests. Probably the simplest compromise is to present gross air specific impulse for sonic discharge conditions which can be easily converted to fuel specific impulse, etc. Gross air specific impulse is defined as:

$$I_{sp_a} = \frac{F}{\overset{\circ}{w}_a} \tag{22}$$

At the outset of this development, it was stated that air was metered by a flow rate control system. As with any "real" piece of apparatus, it is subject to systematic error, and, therefore, must be calibrated. The air flow control system is composed of an automatic pressure regulating system and a sonic Venturi meter. Schematically, the system is arranged as follows:



Air contained in the air storage reservoir is admitted to the Venturi meter at a constant pressure, p_{t_0}, usually sufficiently high to cause the meter to operate at nominally choked conditions. Thus, the weight flow of air to a first approximation is directly proportional to the total pressure, p_{t_0}, the area A_0 and inversely proportional to the square root of the total temperature, T_{t_0}. Since downstream impedances may cause small deviations from "choked" conditions at the Venturi and the heat exchanger which connects the reservoir discharge air temperature is subject to drift, the quantities p_{t_0}, p_0, T_{t_0} are continuously monitored. Thus, the air weight flow delivered by the system at any instant is given by the formula:

$$\dot{w}_a = K_0 A_0 \frac{p_{t_0}}{\sqrt{T_{t_0}}} \sqrt{\frac{\gamma}{R}}\, M_0 \left(1 + \frac{\gamma - 1}{2} M_0^2\right)^{-\frac{\gamma + 1}{2(\gamma - 1)}} \tag{23}$$

where

$$M_0^2 = \frac{2}{\gamma - 1}\left[\left(\frac{p_{t_0}}{p_0}\right)^{\frac{\gamma - 1}{\gamma}} - 1\right]$$

K_0 = discharge coefficient

Recalling that Equation 15 contains a discharge coefficient related to the flow leaving the exhaust nozzle at Station (5), it is clear that this coefficient and the Venturi coefficient form the calibration parameters of the system. Two independent equations can be written for these coefficients providing an additional measurement is made to determine the average total pressure in the exhaust. This is accomplished during a calibration test by means of a total pressure rake located on the exit plane of the exhaust. With the test burner in place, air at test conditions is passed through the apparatus but no fuel is admitted. The assumption made is that the velocity distribution in the exhaust is not primarily a function of the combustion process but of the duct and apparatus geometry. This assumption is born out by the total pressure profiles obtained in the exhaust duct during combustion.[1] The profiles have substantially the same shape when there is no combustion.

Thus the discharge coefficients can be determined using the following two equations:

$$K_0 = \frac{F - A_5\left[p_{t_5}\left(\frac{\gamma+1}{2}\right)^{-\frac{\gamma}{\gamma-1}} - p_a\right]}{\mathring{w}_{a_0}\sqrt{\frac{2\gamma R T_{t_0}}{g(\gamma+1)}}} \tag{24}$$

$$K_E = \frac{K_0 \mathring{w}_{a_0}\sqrt{T_{t_5}}}{p_{t_5} A_5}\sqrt{\frac{\gamma}{R}}\left[\frac{\gamma+1}{2}\right]^{\frac{\gamma+1}{2(\gamma-1)}} \tag{25}$$

where

$$T_{t_5} = T_{t_1} - \frac{Q_{34}(\gamma-1)}{\gamma R \mathring{w}_a}$$

$\mathring{w}_{a_0}$ = air weight flow for $K_0 = 1$

[1] See Figure 48 - Bare Duct Pressure Calibration and Appendix III.

APPENDIX III

TABLES OF DATA AND PLOTS OF COMBUSTION EFFICIENCY VERSUS EQUIVALENCE RATIO FOR COMBUSTION TESTS OF BORON SLURRY FUELS IN THE 3.5-INCH MICRO-RAMJET EQUIPPED WITH PARTICLE MILL INJECTION

TABLE XXXII

COMBUSTION EFFICIENCY VERSUS FUEL-TO-AIR RATIO FOR SLURRY OF 73 PER CENT BALL-MILLED BORON IN JP-4 CARRIER, TESTED IN THE 3.5-INCH MICRO-RAMJET TEST ENGINE. INLET CONDITIONS MACH 2.5 AT SEA LEVEL.[1] (FUEL ATOMIZED BY PARTICLE MILL USING ABOUT 10 PER CENT OF THE AIR). TEST NO. 1.

FUEL-TO-AIR RATIO lb/lb	COMBUSTION EFFICIENCY FROM THRUST MEASUREMENT	COMBUSTION EFFICIENCY FROM CHEMICAL ANALYSIS OF EXHAUST SAMPLES	
		ASSUMING CARRIER EFFICIENCY SAME AS THAT OF BORON	ASSUMING COMPLETE CARRIER COMBUSTION
0.0060	0.720	0.746	0.81
0.0083	0.486	0.511	0.62
0.0115	0.458	0.430	0.5[illegible]
0.0142	0.420	0.404	0.54
0.0162	0.389	0.337	0.49
0.0193	0.330	0.301	0.46
0.0204	0.340	0.254	0.42
0.0216	0.299	0.180	0.3[illegible]
0.0229	0.272	0.178	0.3[illegible]

1 Actual inlet conditions, air flow rates, and thrust levels are contained in Table XXXIII.

TABLE XXXIII

Test Conditions and Total Thrust Levels For
Jet Test of Slurry of 73 Per Cent
Boron in JP-4 (Test No. 1)

POINT NUMBER	FUEL-TO-AIR RATIO lb/lb	T_{T_1} °R	P_{T_1} psia	AIR FLOW RATE lb/sec	OBSERVED TOTAL THRUST* lb
1	0.0000	1036	151.0	9.65	500
2	0.0083	1074	155.0	10.12	594
3	0.0115	1093	156.0	9.70	650
4	0.0142	1109	157.7	9.65	671
5	0.0162	1122	160.0	9.58	666
6	0.0193	1132	164.5	9.52	660
7	0.0204	1138	166.0	9.60	643
8	0.0216	1138	166.5	9.61	638
9	0.0229	1142	166.0	9.60	647

* Corrected for vertical component of force caused by lengthening of air delivery duct.

TABLE XXXIV

COMBUSTION EFFICIENCY VERSUS FUEL-TO-AIR RATIO FOR SLURRY OF 64 PER CENT BALL-MILLED BORON, 16 PER CENT $B_{13}P_2$ IN SO_2-EXTRACTED PARAFFINIC KEROSENE CARRIER, TESTED IN THE 3.5-INCH MICRO-RAMJET TEST ENGINE. INLET CONDITIONS[1] - MACH 2.5 AT SEA LEVEL. (FUEL ATOMIZED BY PARTICLE MILL USING ABOUT 10 PER CENT OF THE AIR).
TEST NO. 2.

FUEL-TO-AIR RATIO lb/lb	COMBUSTION EFFICIENCY FROM THRUST MEASUREMENTS	COMBUSTION EFFICIENCY FROM CHEMICAL ANALYSIS OF EXHAUST SAMPLES	
		ASSUMING CARRIER EFFICIENCY SAME AS THAT OF BORON	ASSUMING COMPLETE CARRIER COMBUSTION
0.0067	0.127	--	--
0.0106	0.103	0.163	0.30
0.0139	0.206	0.197	0.33
0.0153	0.152	0.126	0.27
0.0177	0.171	0.102	0.25
0.0190	0.128	0.096	0.24
0.0230	0.050	0.171	0.31

1 Actual inlet conditions, air flow rates, and thrust levels are presented in Table XXXV.

TABLE XXXV

Test Conditions and Total Thrust Levels For Micro-Ramjet Test of Slurry of 64 Per Cent Boron, 16 Per Cent $B_{13}P_2$ In SO_2-Extracted Paraffinic Kerosene (Test No. 2)

POINT NUMBER	FUEL-TO-AIR RATIO lb/lb	T_{T_1} °R	P_{T_1} psia	AIR FLOW RATE lb/sec	OBSERVED TOTAL THRUST* lb
1	0.0067	845	109	8.65	556
2	0.0106	901	120	8.74	590
3	0.0139	925	129	8.77	655
4	0.0153	978	130	8.79	650
5	0.0177	874	125	8.81	645
6	0.0190	874	127	8.88	630
7	0.0230	876	124	8.90	594

* Corrected for vertical component of force caused by lengthening of air delivery duct.

TABLE XXXVI

COMBUSTION EFFICIENCY VERSUS FUEL-TO-AIR RATIO FOR SLURRY OF 75 PER CENT BALL-MILLED BORON IN ISOPROPANOL, TESTED IN THE 3.5-INCH MICRO-RAMJET TEST ENGINE. INLET CONDITIONS[1] - MACH 2.5 AT SEA LEVEL. (FUEL ATOMIZED BY PARTICLE MILL USING ABOUT 10 PER CENT OF THE AIR). TEST NO. 3.

FUEL-TO-AIR RATIO lb/lb	COMBUSTION EFFICIENCY FROM THRUST MEASUREMENTS	COMBUSTION EFFICIENCY FROM CHEMICAL ANALYSIS OF EXHAUST SAMPLES	
		ASSUMING CARRIER EFFICIENCY SAME AS THAT OF BORON	ASSUMING COMPLETE CARRIER COMBUSTION
0.0096	0.590	0.617	0.68
0.0129	0.491	0.517	0.60
0.0149	0.449	0.410	0.50
0.0163	0.403	0.352	0.45
0.0177	0.344	0.268	0.39
0.0192	0.328	0.227	0.35
0.0207	0.266	0.194	0.32

1 Actual inlet conditions, air flow rates, and thrust levels are presented in Table XXXVII.

TABLE XXVII

Test Conditions and Total Thrust Levels For Micro-Ramjet Test of Slurry of 75 Per Cent Boron in Isopropanol (Test No. 3)

POINT NUMBER	FUEL-TO-AIR RATIO lb/lb	T_{T_1} °R	P_{T_1} psia	AIR FLOW RATE lb/sec	OBSERVED TOTAL THRUST* lb
1	0.0096	881	145.5	9.33	760
2	0.0129	879	150.0	9.33	777
3	0.0149	878	151.0	9.35	786
4	0.0163	882	151.0	9.38	787
5	0.0177	876	153.0	9.45	780
6	0.0192	877	153.0	9.41	783
7	0.0207	874	149.0	9.43	760

* Corrected for vertical component of thrust caused by lengthening of air delivery duct.

TABLE XXXVIII

COMBUSTION EFFICIENCY VERSUS FUEL-TO-AIR RATIO FOR SLURRY OF 70 PER CENT BALL-MILLED HIGH PURITY, ULTRA-FINE BORON IN JP-4, TESTED IN THE 3.5-INCH MICRO-RAMJET TEST ENGINE. INLET CONDITIONS[1] - MACH 2.5 AT SEA LEVEL. (FUEL ATOMIZED BY PARTICLE MILL USING ABOUT 10 PER CENT OF THE AIR). TEST NO. 4.

FUEL-TO-AIR RATIO lb/lb	COMBUSTION EFFICIENCY FROM THRUST MEASUREMENTS	COMBUSTION EFFICIENCY FROM CHEMICAL ANALYSIS OF EXHAUST SAMPLES	
		ASSUMING CARRIER EFFICIENCY SAME AS THAT OF BORON	ASSUMING COMPLETE CARRIER COMBUSTION
0.0058	0.682	0.713	0.79
0.0087	0.589	0.614	0.71
0.0113	0.513	0.524	0.65
0.0130	0.460	0.451	0.59
0.0142	0.416	0.363	0.53
0.0158	0.368	0.324	0.49
0.0169	0.372	0.273	0.45

1 Actual inlet conditions, air flow rate, and thrust levels are presented in Table XXXIX.

TABLE XXXIX

Test Conditions and Total Thrust Levels For
Micro-Ramjet Test of Slurry of 70 Per Cent
High Purity, Ultra-Fine Boron in JP-4 (Test No. 4)

POINT NUMBER	FUEL-TO-AIR RATIO lb/lb	T_{T_1} °R	P_{T_1} psia	AIR FLOW RATE lb/sec	OBSERVED TOTAL THRUST* lb
1	0.0058	879	128	9.30	716
2	0.0087	893	143	9.38	766
3	0.0113	888	150	9.41	781
4	0.0130	893	152	9.[illegible]	790
5	0.0142	893	152	9.50	791
6	0.0158	893	154	9.54	792
7	0.0169	894	155	10.50	820

* Corrected for vertical component of thrust caused by lengthening of air supply duct.

TABLE XL

COMBUSTION EFFICIENCY VERSUS FUEL-TO-AIR RATIO FOR SLURRY CONTAINING 75 PER CENT BALL MILLED SUBMICRON BORON IN JP-4 CARRIER, TESTED IN THE 3.5-INCH MICRO-RAMJET TEST ENGINE. INLET CONDITIONS[1] - MACH 2.5 AT SEA LEVEL (FUEL ATOMIZED BY PARTICLE MILL USING ABOUT 10 PER CENT OF THE AIR). TEST NO. 6.

FUEL-TO-AIR RATIO lb/lb	COMBUSTION EFFICIENCY FROM THRUST MEASUREMENTS	COMBUSTION EFFICIENCY FROM CHEMICAL ANALYSIS OF EXHAUST SAMPLES	
		ASSUMING CARRIER EFFICIENCY SAME AS THAT OF BORON	ASSUMING COMPLETE CARRIER COMBUSTION
0.0064	0.455	0.419	0.56
0.0097	0.366	0.386	0.535
0.0130	0.314	0.338	0.50
0.0146	0.341	0.333	0.495
0.0163	0.303	0.286	0.46
0.0178	0.283	0.248	0.43
0.0194	0.260	0.200	0.385
0.0210	0.246	0.174	0.375

1 Actual inlet conditions, air flow rates, and thrust levels are presented in Table XLI.

TABLE XLI

Test Conditions and Total Thrust Levels for Micro-Ramjet
Test of Slurry of 75 Per Cent Submicron Boron in JP-4 (Test No. 6)

POINT NUMBER	FUEL-TO-AIR RATIO lb/lb	T_{T_1} °R	P_{T_1} psia	AIR FLOW RATE lb/sec	OBSERVED TOTAL THRUST* lb
1	0.0064	787	123	8.87	624
2	0.0097	837	136	8.93	664
3	0.0130	878	145	8.92	691
4	0.0146	876	153	8.96	728
5	0.0163	874	152	9.00	716
6	0.0178	878	153	9.03	723
7	0.0194	875	154	9.01	725
8	0.0210	876	154	9.05	726

* Corrected for vertical component of thrust caused by lengthening of air supply duct.

TABLE XLII

COMBUSTION EFFICIENCY VERSUS FUEL-TO-AIR RATIO FOR SLURRY CONTAINING 65 PER CENT WASHED BORON, 35 PER CENT ISOPROPANOL, TESTED IN THE 3.5-INCH MICRO-RAMJET TEST ENGINE. INLET CONDITIONS[1] - MACH 2.5 AT SEA LEVEL. (FUEL ATOMIZED BY PARTICLE MILL USING ABOUT 10 PER CENT OF THE AIR). TEST NO. 7.

FUEL-TO-AIR RATIO lb/lb	COMBUSTION EFFICIENCY FROM THRUST MEASUREMENTS	COMBUSTION EFFICIENCY FROM CHEMICAL ANALYSIS OF EXHAUST SAMPLES	
		ASSUMING CARRIER EFFICIENCY SAME AS THAT OF BORON	ASSUMING COMPLETE CARRIER COMBUSTION
0.0049	0.796	0.795	0.84
0.0079	0.746	0.862	0.90
0.0087	0.826	0.825	0.87

1 Actual inlet conditions, air flow rates, and thrust levels are presented in Table XLIII.

TABLE XLIII

Test Conditions and Total Thrust Levels for Micro-Ramjet Test of Slurry of 65 Per Cent Washed Boron in Isopropanol (Test No. 7)

POINT NUMBER	FUEL-TO-AIR RATIO lb/lb	T_{T_1} °R	P_{T_1} psia	AIR FLOW RATE lb/sec	OBSERVED TOTAL THRUST* lb
1	0.0049	885	142	9.56	726
2	0.0079	881	150	9.57	780
3	0.0087	879	156	9.68	820

* Corrected for vertical component of force caused by lengthening of air supply duct.

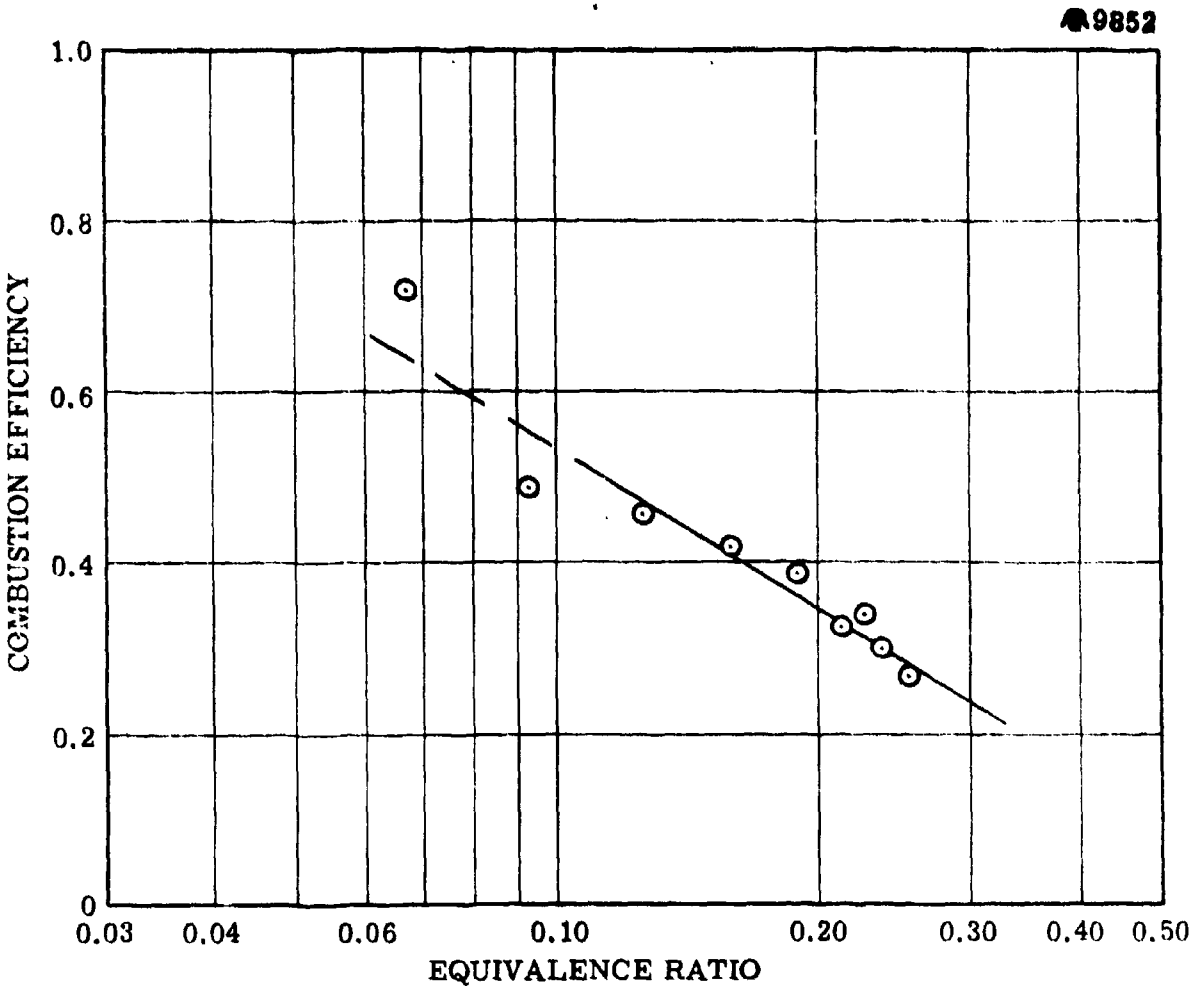


Figure 71. Combustion Efficiency Versus Equivalence Ratio for Test No. 1, using a JP-4 Based Boron Slurry Containing 73 Per Cent Solids. Tested in the 3.5-inch Micro-Ramjet Engine with Particle Mill Injection. Inlet Conditions - Mach 2.5 at Sea Level, Cold Day.

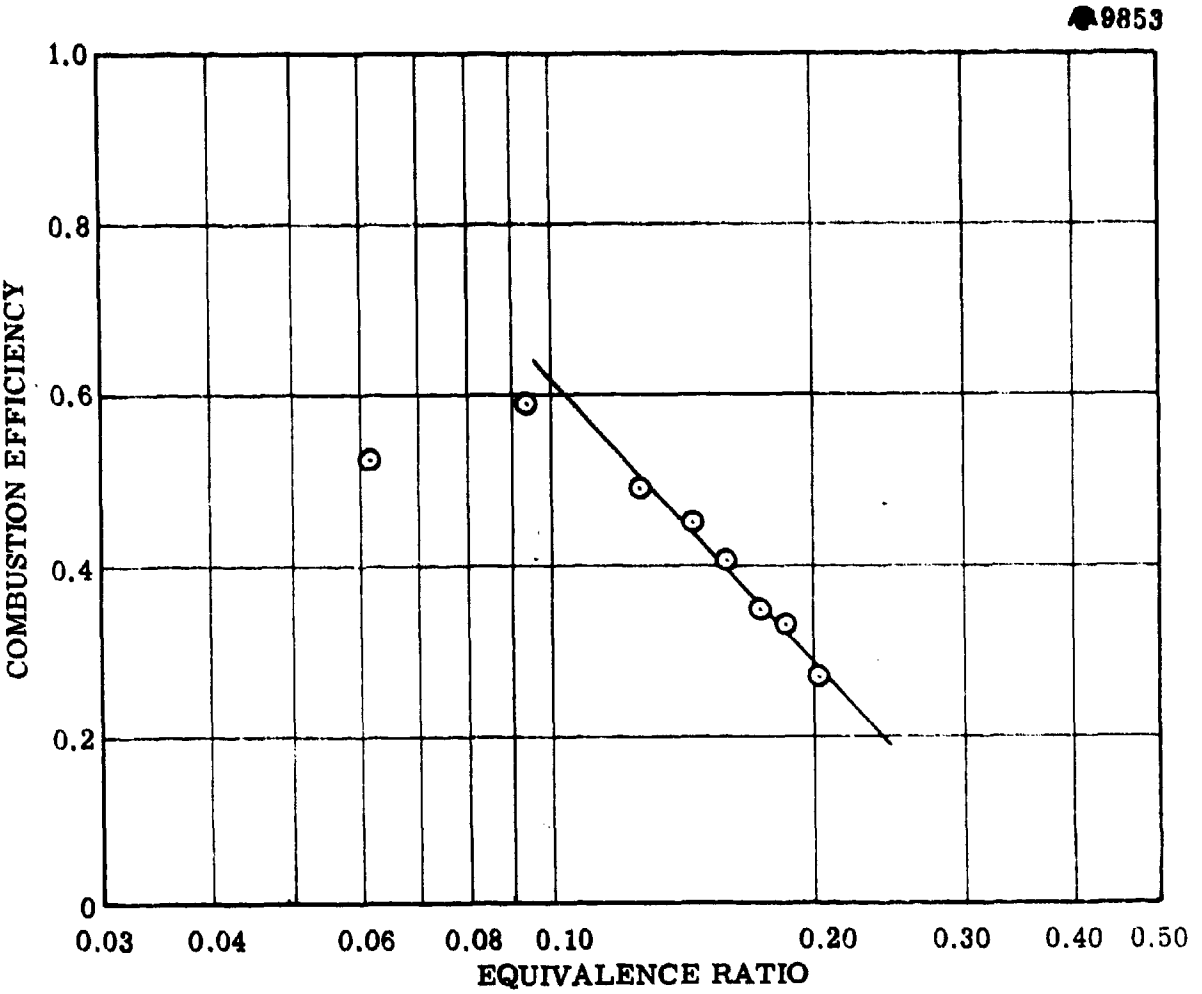


Figure 72. Combustion Efficiency Versus Equivalence Ratio for Test No. 3, using a Slurry of 75 Per Cent Boron in Isopropanol. Tested in the 3.5-inch Micro-Ramjet Engine with Particle Mill Injection. Inlet Conditions - Mach 2.5 at Sea Level, Cold Day.

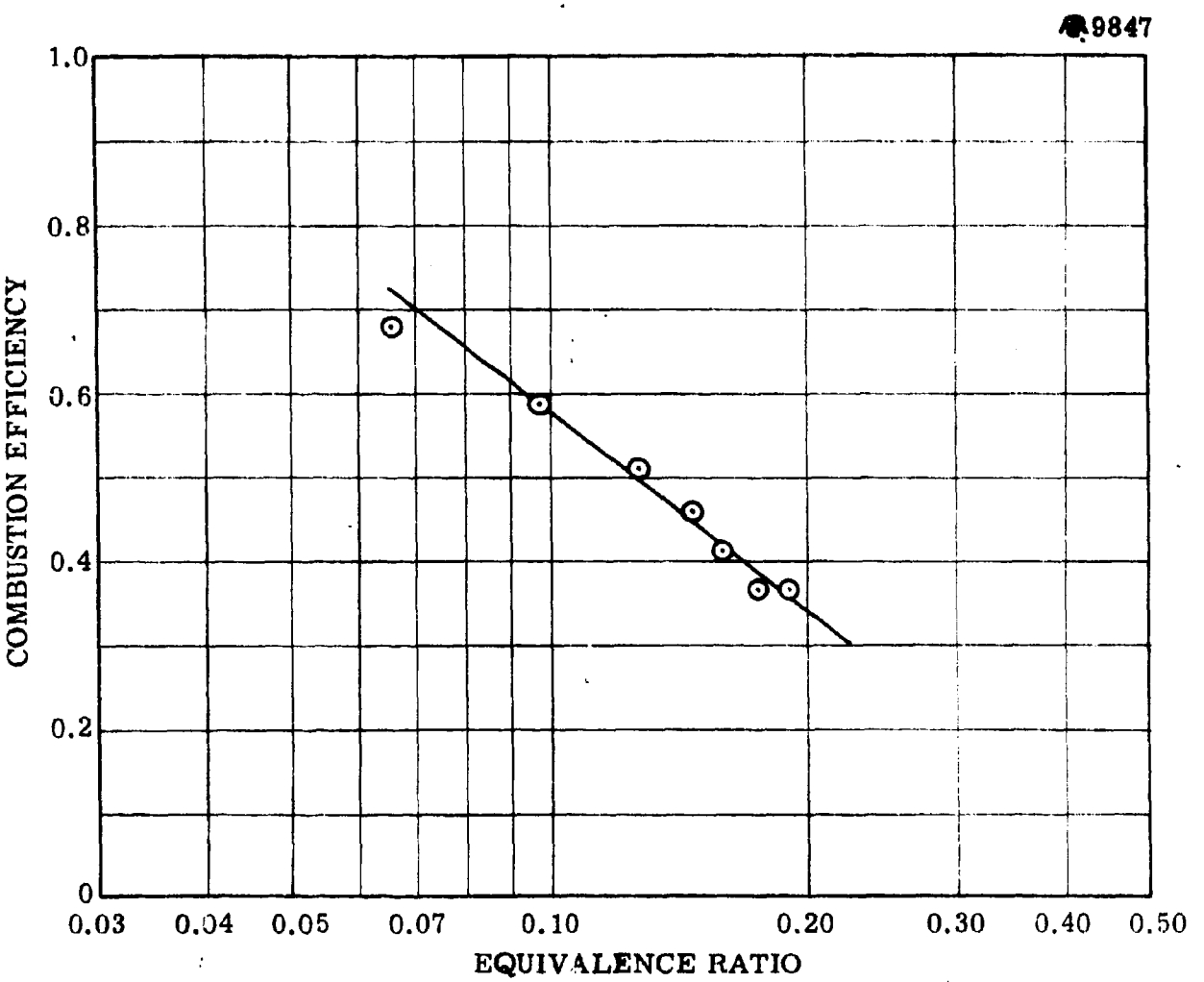


Figure 73. Combustion Efficiency Versus Equivalence Ratio for Test No. 4, using a JP-4 Based Boron Slurry Containing 70 Per Cent High Purity, Ultra-Fine Boron. Tested in the 3.5-inch Micro-Ramjet Engine with Particle Mill Injection. Inlet Conditions - Mach 2.5 at Sea Level, Cold Day.

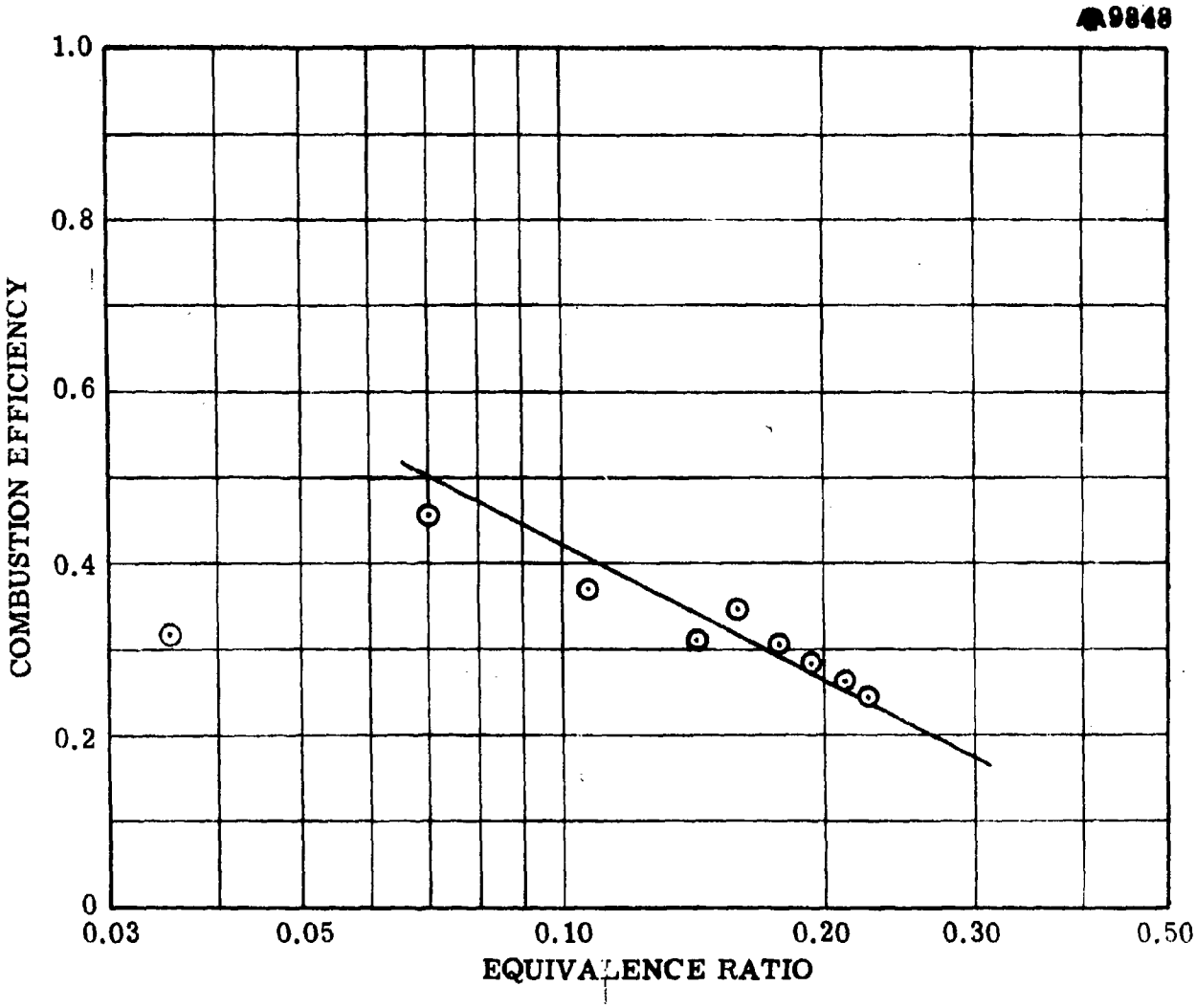


Figure 74. Combustion Efficiency Versus Equivalence Ratio for Test No. 6, using a JP-4 Based Boron Slurry Containing 75 Per Cent Submicron Boron Tested in the 3.5-inch Micro-Ramjet Engine with Particle Mill Injection. Inlet Conditions - Mach 2.5 at Sea Level, Cold Day.

TABLE XLIV

Test Conditions and Total Thrust Levels
For Micro-Ramjet Test of Slurry of 73 Per Cent
Boron In JP-4 (Test No. 13)

POINT NUMBER	FUEL-TO-AIR RATIO lb/lb	T_{T_1} °R	P_{T_1} psia	AIR FLOW RATE lb/sec	OBSERVED TOTAL THRUST lb
1	0.0065	880	139.2	9.24	685
2	0.0082	880	143.7	9.26	725
3	0.0110	880	144.5	9.28	730
4	0.0139	881	148.0	9.27	767
5	0.0168	882	150.7	9.30	786
6	0.0196	880	152.4	9.30	801

TABLE XLV

Pressure Rake Data (P_{t_5}) from Micro-Ramjet Test No. 13 with Fuel of 73 Per Cent Boron in JP-4 at Inlet Conditions of Mach 2.5 at Sea Level, Cold Day (Inlet Station Positions are Shown on Figure 48 of this Report)

	Measured Pressure, psia						
Fuel-to-Air Ratio lb/lb	Static Pressure	P_{t_4} Station 1	P_{t_4} Station 2	P_{t_4} Station 3	P_{t_4} Station 4	P_{t_4} Station 5	Average (P_{t_5})
0.0065	89.1	100.3	102.9	103.1	103.0	106.0	103.6
0.0082	94.1	105.2	108.5	108.5	109.4	109.7	108.2
0.0110	95.5	106.4	108.5	108.5	113.1	113.3	110.0
0.0139	98.4	108.3	114.2	108.7	115.6	115.2	112.4
0.0168	100.3	111.4	116.0	111.7	119.9	120.2	115.3
0.0196	102.8	115.0	118.0	113.5	120.6	122.0	117.3

TABLE XLVI

Test Conditions and Total Thrust Levels For Micro-Ramjet Test of Slurry of 75 Per Cent Boron In Isopropanol (Test No. 14)

POINT NUMBER	FUEL-TO-AIR RATIO lb/lb	T_{T_1} °R	P_{T_1} psia	AIR FLOW RATE lb/sec	OBSERVED TOTAL THRUST lb
1	0.0061	901	133.6	8.83	621
2	0.0094	904	141.5	8.83	682
3	0.0127	898	146.7	8.96	717
4	0.0156	897	147.7	8.95	726
5	0.0187	900	147.7	8.95	728
6	0.0212	901	147.7	8.96	728

TABLE XLVII

Pressure Rake Data (P_{t_5}) from Micro-Ramjet Test No. 14 with Fuel of 75 Per Cent Boron in Isopropanol at Inlet Conditions of Mach 2.5 at Sea Level, Cold Day (Inlet Station Positions are Shown on Figure 48 of this Report)

	Measured Pressure, psia						
Fuel-to-Air Ratio lb/lb	Static Pressure	P_{t_4} Station 1	P_{t_4} Station 2	P_{t_4} Station 3	P_{t_4} Station 4	P_{t_4} Station 5	Average P_{t_5}
0.0061	83.6	91.7	96.3	96.1	97.3	100.5	96.4
0.0094	91.6	102.2	105.2	104.3	106.1	111.4	105.8
0.0127	95.4	105.8	109.6	108.0	113.0	117.0	110.7
0.0156	95.9	107.7	110.9	108.7	115.0	118.9	112.2
0.0187	96.6	107.7	113.4	107.4	115.4	120.3	114.4
0.0212	95.9	107.7	114.7	109.9	114.3	125.3	115.0

TABLE XLVIII

Test Conditions and Total Thrust Levels For Micro-Ramjet Test of Slurry of 80 Per Cent Boron In Isooctane (Test No. 15)

POINT NUMBER	FUEL-TO-AIR RATIO lb/lb	T_{T_1} °R	P_{T_1} psia	AIR FLOW RATE lb/sec	OBSERVED TOTAL THRUST lb
1	0.0033	899	137	9.15	648
2	0.0049	895	140.5	9.07	681
3	0.0060	891	140.5	9.10	705
4	0.0064	895	145.0	9.11	728
5	0.0081	895	140.5	9.12	753
6	0.0097	891	148.6	9.08	768

TABLE XLIX

Pressure Rake Data (P_{t_5}) from Micro-Ramjet Test No. 15 with Fuel of 30 Per Cent Boron in Isooctane at Inlet Conditions of Mach 2.5 at Sea Level, Cold Day (Inlet Station Positions are Shown on Figure 48 of this Report)

Fuel-to-Air Ratio lb/lb	Measured Pressure, psia						
	Static Pressure	P_{t_4} Station 1	P_{t_4} Station 2	P_{t_4} Station 3	P_{t_4} Station 4	P_{t_4} Station 5	Average (P_{t_5})
0.0033	83.6	95.4	99.5	99.5	98.9	102.7	99.2
0.0049	88.6	101.6	104.5	105.1	105.2	107.1	104.7
0.0060	89.9	103.4	103.9	103.8	105.2	107.7	104.8
0.0064	94.2	106.5	109.0	112.0	110.2	113.3	110.2
0.0081	96.0	108.4	114.0	111.4	115.2	117.0	113.2
0.0097	97.2	110.3	114.1	112.0	115.2	116.0	113.5

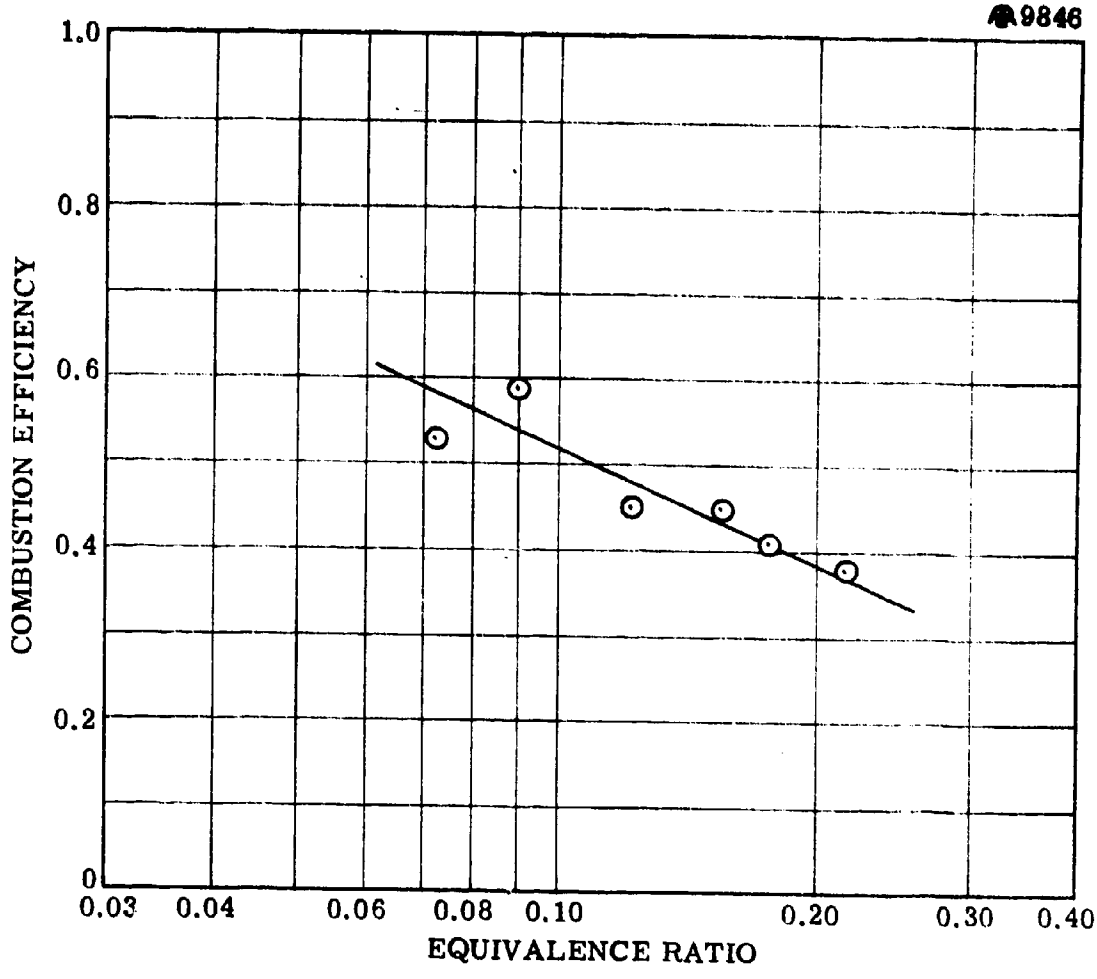


Figure 75. Combustion Efficiency Versus Equivalence Ratio for Test No. 13, using a JP-4 Based Boron Slurry Containing 73 Per Cent Solids Tested in the 3.5-inch Micro-Ramjet Engine Equipped with the Total Pressure Rake. Inlet Conditions - Mach 2.5 at Sea Level, Cold Day.

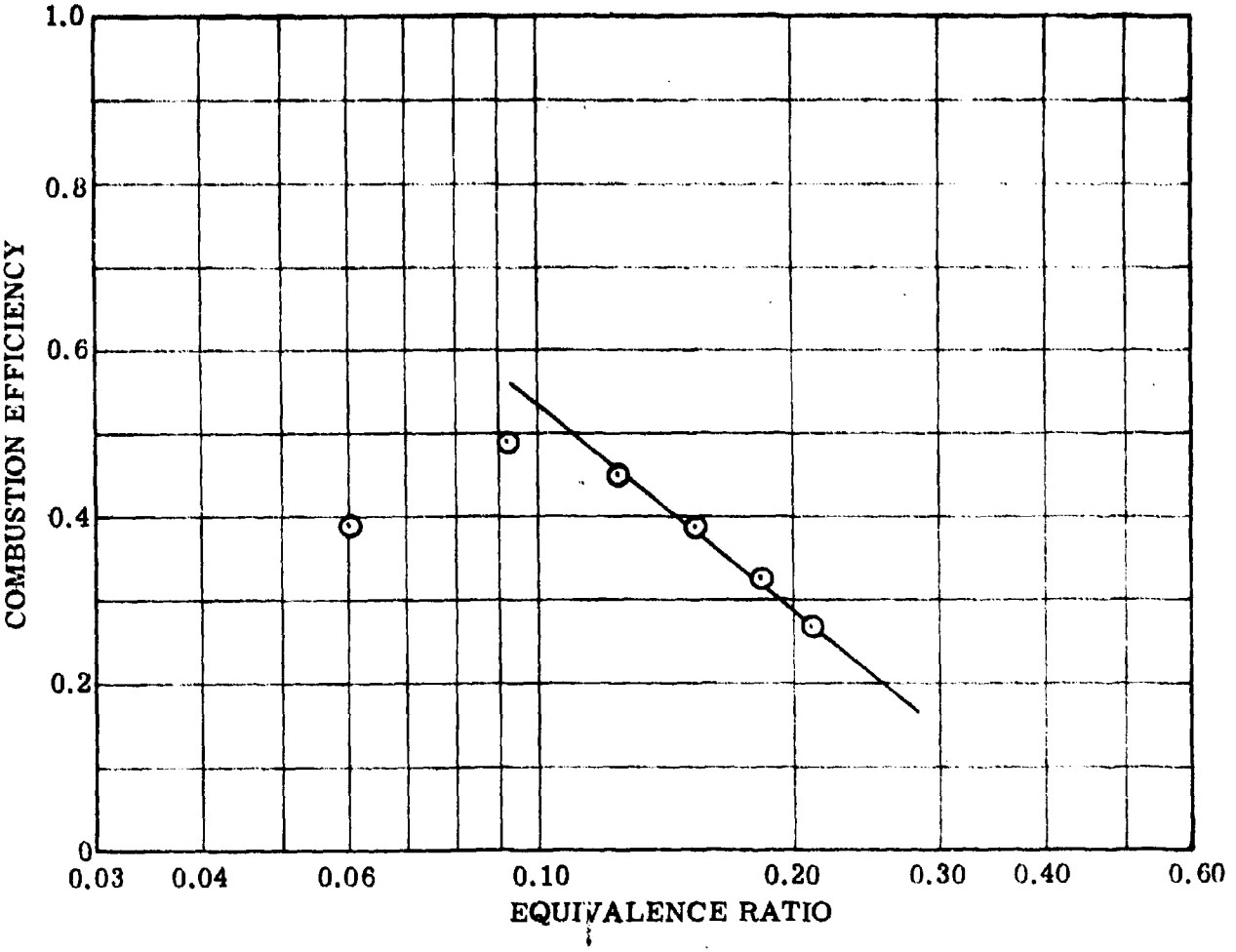


Figure 76. Combustion Efficiency Versus Equivalence Ratio for Test No. 14, using an Isopropanol-Based Boron Slurry Containing 75 Per Cent Solids, Tested in the 3.5-inch Micro-Ramjet Engine with and Without the Total Pressure Rake. Inlet Conditions - Mach 2.5 at Sea Level, Cold Day.

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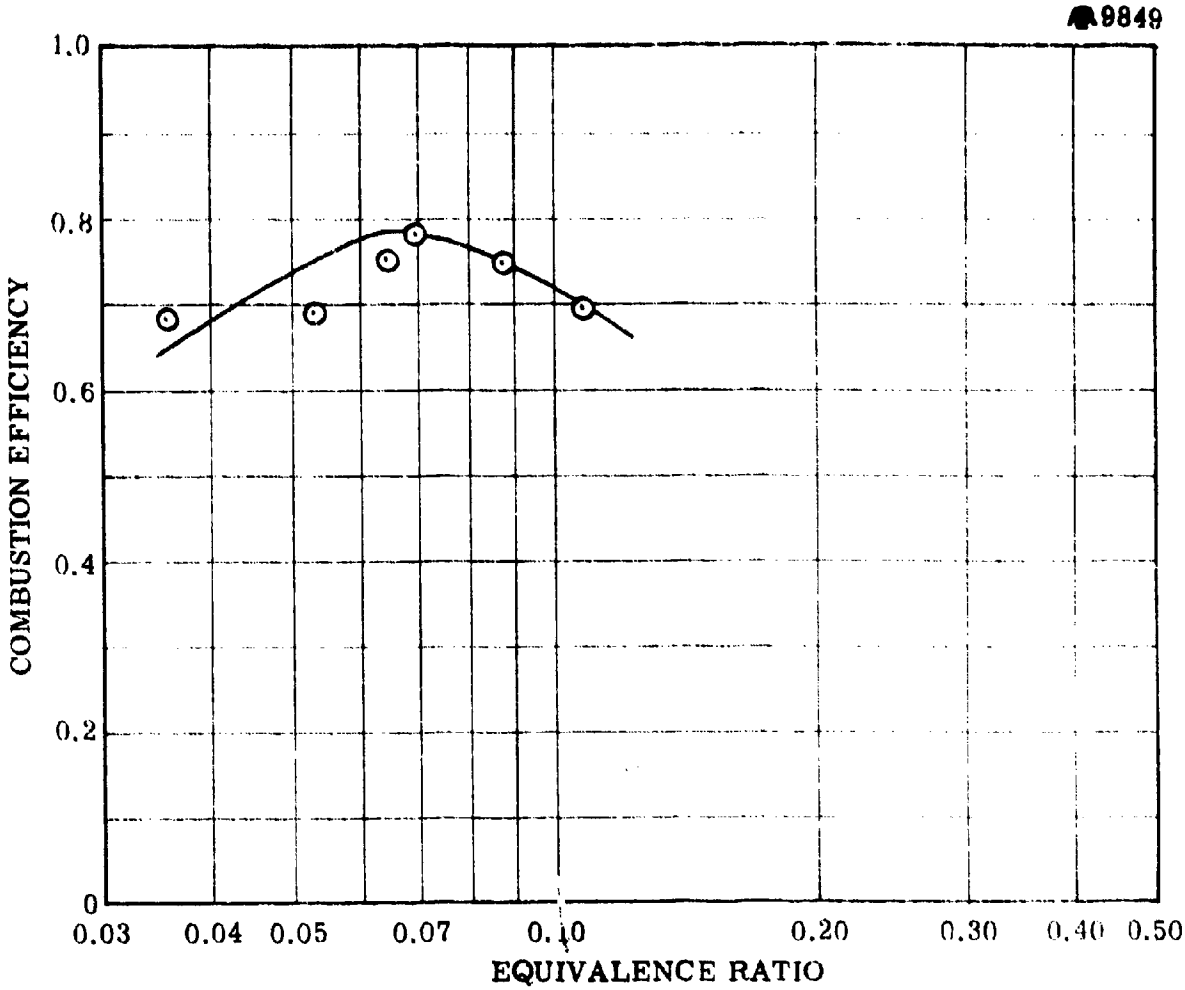

Figure 77. Combustion Efficiency Versus Equivalence Ratio for Test No. 15, using an Isooctane-Based Boron Slurry Containing 80 Per Cent Solids, Tested in the 3.5-inch Micro-Ramjet Engine Equipped with the Total Pressure Rake. Inlet Conditions - Mach 2.5, Sea Level, Cold Day.

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11 SUPPLEMENTARY NOTES	12. SPONSORING MILITARY ACTIVITY AF Systems Command, Research and Technology Div., Aero Propulsion Lab., Wright-Patterson AFB, Ohio

13 ABSTRACT

This program was concerned with the development, characterization and combustion testing of advanced boron slurry fuels for use in low-altitude ramjet-powered missiles. Three types of boron were used: commercial grade, submicron; and ultra-fine, high purity boron. Through extensive ball-milling of the submicron and ultra-fine powders, slurries could be formulated (in ungelled JP-4 carrier) which were competitive with standard commercial-grade formulations in volumetric heat release, rheology, and stability. Other formulation work resulted in the optimization of a 1965 "workhorse" formulation (basic formulation of 73 per cent ball-milled boron in gelled JP-4) and a slurry of washed boron in isopropanol which can be loaded to a maximum solids content of about 80 per cent. (C)

The most critical trade-off among slurry properties is between storage stability and rheology (yield stress and viscosity) at low temperatures. Based on work at the University of Dayton Research Institute, the apparent viscosities of "standard", shelf-storable slurries of 73 per cent boron in JP-4 and 75 per cent boron in isopropanol at 100 sec^{-1} shear rate and -65°F are about 5,000 poise and 4,000 poise, respectively. Reduction of these values appears to be one of the most immediate problems in future boron slurry development. (C)

A particle (agglomerate) size distribution of one to 50 microns was found in slurries containing ball-milled commercial boron. Atomization in the particle mill resulted in mostly particles between 25 and 100 microns in diameter; and atomization in a dual-fluid injector designed for use with the micro-ramjet produced particles

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14 KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Fuels						
Slurry Fuels						
Boron						
Ramjet						
Combustion						
Atomization						

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13. ABSTRACT (Continued)

mostly between 10 and 50 microns in diameter. (C)

Combustion tests were performed in an ambient-pressure combustor and a 3.5-inch micro-ramjet engine equipped with a particle mill or with a dual-fluid injector. The results of the particle-mill tests established a base-line for comparison of micro-ramjet combustion data with data from the Marquardt test engine. Trends observed in combustion performance as a function of slurry properties included enhancement of performance corresponding to : a more volatile carrier; smaller particle size resulting from atomization; and (possibly) decontamination of the surface. With the dual-fluid injector the slurry containing 70 per cent ultra-fine, high-purity boron performed best by far, indicating a strong enhancement due to the small particle size when the slurry is well atomized. (C)

Very little combustion data were obtained with slurries containing 80 per cent solids, because of dilation of these slurries in the feed system. The two most promising formulations at present are 73 per cent ball-milled boron in gelled JP-4, and 75 per cent ball-milled boron in isopropanol. These two slurries performed similarly in the particle-mill-equipped micro-ramjet engine. (C)